Journal of Alloys and Compounds 570 (2013) 114–118

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Control of hydrogen storage properties of $(La,Ce,Nd,Pr)(Ni,Co,Mn,Al)_5$ alloys with microstructural parameters

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ARTICLE INFO

Article history:
Received 15 February 2013
Received in revised form 12 March 2013
Accepted 12 March 2013
Available online 26 March 2013

Keywords:
Hydrogen storage materials
Rare earth compounds
Pressure–composition isotherms
Plateau pressure
X-ray diffraction

ABSTRACT

Atomic radius factor—a factor related to the composition in $(La,Ce,Nd,Pr)(Ni,Co,Mn,Al)_5$ alloys, was deduced and used to prepare low-cost alloys. The plateau pressure and hydrogen storage capacity were changed with respect to the crystal lattice volume of the $(La,Ce,Nd,Pr)(Ni,Co,Mn,Al)_5$, which could be controlled by changing the ratio of the elements in the alloy. Therefore, the plateau pressure and hydrogen storage capacity were adjusted by using the atomic radius factor, defined as the summation of the multiplication of the atomic radii and molar ratios of each element in the alloy. Finally, low-cost alloys (Nd-free/Ce-rich) were designed and prepared using the atomic radius factor. By simultaneously increasing the amounts of Ce and Mn in the alloy, the atomic radius factor and the crystal lattice volume of the alloy could be made similar to those of a commercial alloy. Consequently, it is possible to control the hydrogen storage properties and to prepare low-cost alloys with hydrogen storage properties similar to those of commercial alloy using the atomic radius factor.

1. Introduction

Ever since the hydrogen storage properties of $LaNi_5$ alloy were first discovered by Vucht et al. [1], $LaNi_5$ alloy has been studied as a hydrogen storage alloy because of its high volumetric storage density, easy activation, and moderate kinetic properties. However, the $LaNi_5$ alloy has several disadvantages, including low hydrogen capacity, a significant decrease in storage capacity over the cyclic absorption/desorption process, a relatively low plateau pressure, and high cost [2]. Therefore, it has limited application. Many researchers [3–11] have carried out research to improve its properties.

Various properties would be considered for use of $LaNi_5$ alloy because the required properties were different by its usage in $LaNi_5$ alloy. If $LaNi_5$ alloy is used for battery material, the properties like corrosion resistance, pulverizing property, hydrogen storage capacity, plateau pressure, and cycle lifetime are critical and the properties depend on element properties in the alloy. For example, it was found that the partial respective replacement of Ni in $LaNi_5$ by small amounts of Al resulted in a prominent increase in the cycle lifetime without causing much decrease in capacity [12]. And previous studies [13–17] showed that Mn partial substitution for Ni can increase the cell volume, decrease the hydrogen plateau pressure, shorten the activation cycle and improve the high rate discharge ability.

Therefore, substituting La and Ni with other elements in the $LaNi_5$ alloy has been considered an alternative for overcoming its limitations and the effect of the substituted elements on the hydrogen storage properties of the resulting alloy has also been investigated. Van Mal et al. stated that the plateau pressure of the alloy changed when elements such as Y, Er, Gd, or Nd were substituted for La and that both the hydrogen storage capacity and the plateau pressure varied when Pd, Ag, Cu, Co, Fe, or Cr were substituted for Ni [3]. Marshall et al. found that the change in the plateau pressure of the $LaNi_5$ alloy was caused by changes in the crystal lattice volume; they also investigated the relationship between the crystal lattice volume and plateau pressure [4]. They found that the plateau pressure increased as the crystal lattice volume of the alloy decreased.

Thus, many researchers have tried to control the hydrogen storage properties of these alloys by using the relationship between the hydrogen storage properties and the crystal lattice volume [5–11]. In these studies, the crystal lattice volume was increased either by adding elements with a large atomic radii or by ball-milling process. As a result, the hydrogen storage capacity was increased while the plateau pressure was decreased. This is because the use of elements with large atomic radii made available more space for hydrogen absorption and the strain induced by ball-milling increased the crystal lattice volume of the alloy.

In this work, a factor related to the composition in $(La,Ce,Nd,Pr)(Ni,Co,Mn,Al)_5$ alloys, was deduced and used to prepare low-cost alloys. First, the effect of the amount of Ce (the most abundant rare-earth element) on the crystal lattice volume of the

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0925-8388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jallcom.2013.03.124

$LaNi_5$ alloy partly substituted by Ce was investigated by a first-principles calculation. Then, the factor related to the composition for controlling the crystal lattice volume and hydrogen storage properties, were experimentally deduced. Finally, the low-cost alloys (with large amount of Ce, without Nd) with similar properties to those of a commercial alloy were designed and prepared using the factor. The properties, which were discussed in this paper, were limited to plateau pressure and hydrogen storage capacity among various properties of hydrogen storage material.

2. Calculation method

The Vienna ab initio simulation package (VASP) was used to calculate the crystal lattice volume of the (La,Ce)Ni_5 alloys. Exchange–correlation effects were analyzed in the framework of the generalized gradient approximation (GGA) proposed by Perdew and Wang [18]. Integration in the Brillouin zone was performed using the Monkhorst Pack: $7 \times 7 \times 7$ k points for the $2 \times 2 \times 2$ super-cell (83 atoms) model as shown in Fig. 1. To improve the accuracy of the results, we employed a high-energy cutoff energy of 600 eV with an energy convergence of 0.01 eV/Å, and the first-order Methfessel–Paxton method was used for the Fermi-surface smearing to obtain accurate forces. To obtain accurate equilibrium volume, model relaxations were conducted at least three times for each model.

3. Experimental procedure

$(La,Ce,Nd,Pr)(Ni,Co,Mn,Al)_5$ alloys were prepared into button-shaped ingots, each of ~20–30 g, by arc melting under Ar atmosphere. To make alloys with a homogeneous composition, the ingots were turned over and remelted 5 times. The purity and size of the raw materials (Ni,Co,Mn,Al and Misch-metals (La,Ce,Nd,Pr or La,Ce,Pr)) used in this experiment were 99.5% and ~3–20 mm, respectively. The ratios of metals in the starting materials were varied for preparing the alloys and had not only different amounts of Ce but also different crystal lattice volumes, as shown in Table 1.

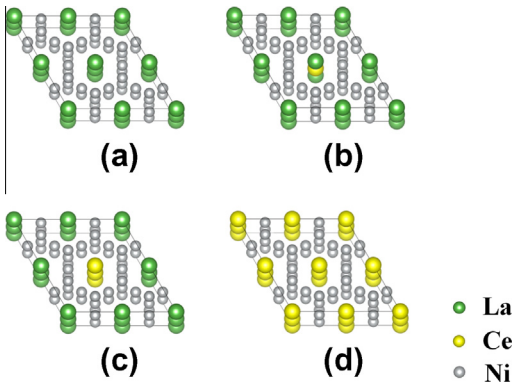

Fig. 1. Schematic diagrams of four supercell models used in this calculation: (a) $LaNi_5$ (b) $(La_{0.875},Ce_{0.125})Ni_5$ (c) $(La_{0.75},Ce_{0.25})Ni_5$ and (d) $CeNi_5$.

Table 1
Ratios of the metals used for preparation $(La,Ce,Nd,Pr)(Ni,Co,Mn,Al)_5$ alloys (wt.%).

	La	Ce	Nd	Pr	Ni	Co	Mn	Al
#1	25.3	4.5	1.4	0.9	54.2	8.1	3.8	1.8
#2	19.8	11.5	–	0.9	54.9	6.2	5.1	1.6
#3	19.7	11.7	–	0.7	54.2	8.1	3.8	1.8
#4	17.2	14.2	–	0.8	54.9	6.2	5.1	1.6
#5	13.0	18.7	–	0.5	54.2	8.1	3.8	1.8
#6	11.0	20.7	–	0.5	54.9	6.2	5.1	1.6
#7	5.2	25.8	–	0.2	54.9	8.2	3.8	1.8
#8	4.8	27.3	–	0.2	54.8	6.2	5.1	1.6

X-ray diffraction patterns from the alloys were acquired using Cu Kα radiation from an X-ray diffractometer (SmartLab, Rigaku, Japan) operating in the Bragg–Brentano geometry with counting time of 5 s and steps of 0.01° in 2θ. In particular, a Si sample (SRM640D, NIST) was used as an internal standard to remove the instrumental error. The compositions of the ingots were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. The pressure–composition (P–C) isotherms of the samples were measured in a Sievert's type apparatus up to 5 MPa pressure.

4. Results and discussion

4.1. Effect of the amount of Ce on the crystal lattice volume of (La,Ce)Ni_5 alloy

Table 2 shows the lattice parameters and crystal lattice volumes of the (La,Ce)Ni_5 alloys obtained from the first-principles calculation. As the content of Ce in the alloys increased, the lattice parameters (a-) decreased. As a result, the crystal lattice volumes of the $LaNi_5$ alloys substituted with Ce are smaller than those of the $LaNi_5$ alloy. This is because the atomic radius of Ce (185 pm) is smaller than that of La (195 pm). Therefore, $(La,Ce,Nd,Pr)(Ni,Co,Mn,Al)_5$ alloy with a larger amount of Ce would have a smaller crystal lattice volume.

4.2. Deduction of the factor for designing the composition

Fig. 2 shows the XRD results for the alloys with the compositions shown in Table 1. The main peak of the alloy moves to a higher angle as the Ce content increases. This means that the crystal lattice volume of the alloy with a higher amount of Ce is smaller than that of the alloy with a lower amount of Ce, as confirmed in the first-principles calculation. This change in the crystal lattice volume influences the hydrogen storage properties of the resulting alloys. When the hydrogen storage properties of the alloys were estimated, it was found that the plateau pressure of the alloys with smaller crystal lattice volumes was higher than that of alloys with higher crystal lattice volumes (Fig. 3). Also, the hydrogen storage

Table 2
Lattice parameters and crystal lattice volumes calculated by first-principles calculation.

	Lattice parameter (Å)		Crystal lattice volume (Å^3)
	a	c	
$LaNi_5$	5.002	3.976	86.154
$(La_{0.875},Ce_{0.125})Ni_5$	4.990	3.981	85.856
$(La_{0.75},Ce_{0.25})Ni_5$	4.974	3.986	85.406
$CeNi_5$	4.883	4.003	82.675

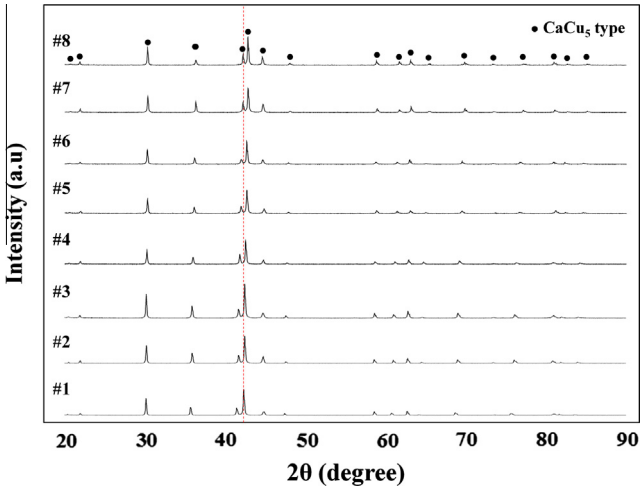

Fig. 2. XRD profiles of $(La,Ce,Nd,Pr)(Ni,Co,Mn,Al)_5$ alloys prepared by arc melting.