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Letter

Hydrogen storage properties of new ternary system alloys: La_2MgNi_9 , $\text{La}_5\text{Mg}_2\text{Ni}_{23}$, $\text{La}_3\text{MgNi}_{14}$

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Abstract

The hydrogen storage properties of the new ternary system alloys, La_2MgNi_9 , $\text{La}_5\text{Mg}_2\text{Ni}_{23}$, $\text{La}_3\text{MgNi}_{14}$, were investigated. As a result, the negative electrode of the $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ alloy ($\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$) showed a large discharge capacity (410 mAh/g), 1.3 times larger than that of AB_5 type alloys. These ternary system alloys were found to be mainly composed of stacked AB_5 and AB_2 structure subunits in a superstructure arrangement. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Hydrogen storage alloy has attracted considerable attention in view of its potential as a new energy storage material. Recently, nickel-metal hydride battery (MH) in which a hydrogen storage alloy is employed as a negative electrode material has become a focus of interest as a candidate consumer-use battery by virtue of its several advantages: high capacity, high resistance to overcharging and overdischarging, capable of performing a high rate charge/discharge, environmental friendliness, and interchangeable with a nickel-cadmium battery [1,2]. However, the capacity of MH battery using LaNi_5 type alloy is approaching its limits, because the repeated improvements to increase the capacity have already realized very high utilization of the intrinsic capacity of the alloy.

For increasing the capacity, the La–Mg–Ni system alloy is one of the most promising candidates. For example, $\text{La}_{1-x}\text{Mg}_x\text{Ni}_2$ alloy is superior to LaNi_5 type alloy or Laves-phase alloys in hydrogen absorption capacity [3]. However, it is pointed out that $\text{La}_{1-x}\text{Mg}_x\text{Ni}_2$ type alloys are subject to a problem in that the hydrogen-releasing rate

is very low due to the high stability with respect to hydrogen [3]. It has been reported that a PuNi_3 system alloy having a composition of Mg_2LaNi_9 has a low discharge capacity [4].

In this work, in order to increase the discharge capacity of the negative electrode, we studied La–Mg–Ni_x ($x=3–3.5$) system alloys using electrochemical methods, and the structure of this alloy system has been investigated to evaluate its applicability to MH batteries.

2. Experimental

$\text{La}_{0.67}\text{Mg}_{0.33}\text{Ni}_{2.5}\text{Co}_{0.5}$, $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$, $\text{La}_{0.75}\text{Mg}_{0.25}\text{Ni}_{3.0}\text{Co}_{0.5}$ alloy ingots were prepared by induction melting under Ar gas at atmospheric pressure. These ingots were mechanically pulverized to 75 μm or less in diameter and preliminary activation with hydrogen was not performed. Crystallographic characterizations of these alloys were carried out by X-ray diffraction at room temperature. The hydrogen absorption–desorption properties of the alloy were investigated by pressure–composition (P–C) isotherms and an electrochemical charge–discharge process. In this process, the hydrogen storage

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alloy powder was mixed with electrolytic copper powder in the weight ratio of 1:3, and then 1 g of this mixture was compressed in a tablet-molding apparatus (inner diameter: 10 mm) with a pressure of 10 tons for 5 min. This pellet was then interposed between Ni gauze, and the portion on the edge was tightly spot-welded to keep the electrochemical contact between the pellet and Ni gauze. Afterwards, a Ni wire was attached to Ni gauze by spot-welding to prepare a hydrogen storage alloy electrode (negative electrode). The negative electrode and counter electrodes (sintered nickel) were dipped in 8 M KOH, and then charge–discharge cycle tests were performed at 25°C. The mercury oxide electrode (Hg/HgO/8 M KOH) was used as a reference electrode. In these charge–discharge cycle tests, the charge was conducted using the current rate of 100 mA/g-hydrogen storage alloy for 5 h. After a 10-min rest, the discharge was conducted using the current rate of 100 mA/g-hydrogen storage alloy until the voltage of the negative electrode against the mercury oxide electrode reached -0.5 V.

3. Results and discussion

In the case of $\text{La}_{1-x}\text{Mg}_x\text{Ni}_2$ alloy, as described above, it is very difficult to desorb hydrogen because of the high stability though the alloy is capable of absorbing a large quantity of hydrogen [3]. For these reasons, we focused on La-Mg-Ni_x ($x=3-3.5$) system alloys. The hydrogen absorption–desorption properties of these alloys were investigated by an electrochemical charge–discharge method. Discharge capacities of La_2MgNi_9 , $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ and $\text{La}_3\text{MgNi}_{14}$ system alloy electrodes are shown in Table 1. Among these alloys, $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy ($\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$) showed a large discharge capacity which is 1.3 times larger than that of LaNi_5 system alloy.

The cyclic trends of discharge capacities of $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy and LaNi_5 system alloy electrodes at 25°C are shown in Fig. 1. $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$ alloy electrode had the discharge capacity at the first cycle and there were few decreases in discharge capacity during the cycle test. The discharge curve of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$ electrode had a wide plateau region during discharge, and no other

Table 1
Discharge capacity of La-Mg-Ni_x ($x=3-3.5$) system alloy

Alloy system	Alloy	Discharge capacity (mAh/g)
La_2MgNi_9 ($\text{La}_{0.67}\text{Mg}_{0.33}\text{Ni}_3$)	$\text{La}_{0.67}\text{Mg}_{0.33}\text{Ni}_{2.5}\text{Co}_{0.5}$	387
$\text{La}_5\text{Mg}_2\text{Ni}_{23}$ ($\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{3.3}$)	$\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$	410
$\text{La}_3\text{MgNi}_{14}$ ($\text{La}_{0.75}\text{Mg}_{0.25}\text{Ni}_{3.5}$)	$\text{La}_{0.75}\text{Mg}_{0.25}\text{Ni}_{3.0}\text{Co}_{0.5}$	390
LaNi_5	$\text{MmNi}_{4.0}\text{Mn}_{0.3}\text{Al}_{0.3}\text{Co}_{0.4}$	320

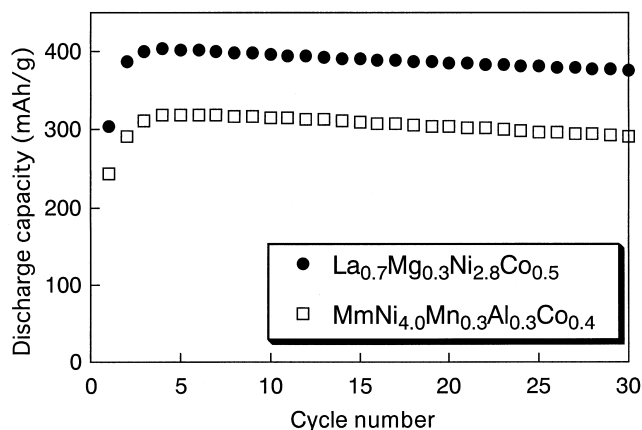


Fig. 1. Discharge capacities of $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy and LaNi_5 system alloy.

potential step attributable to side reactions was observed. This result suggested that only the hydrogen electrode reaction took place in this potential range.

XRD patterns for $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy and LaNi_5 alloy are shown in Fig. 2. $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$ alloy has a pattern quite different from that of LaNi_5 alloy. This profile indicates that $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy is composed of stacked AB_5 and AB_2 structure subunits in a superstructure arrangement, as shown in Fig. 3.

Fig. 4 shows P–C isotherms of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}-\text{H}_2$ system and $\text{MmNi}_{4.0}\text{Mn}_{0.3}\text{Al}_{0.3}\text{Co}_{0.4}-\text{H}_2$ system. It was measured at 60°C in the pressure range of 10^{-3} MPa to 1.0 MPa with a Sieverts' type apparatus. The maximum atomic ratio (H/M) of the $\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}-\text{H}_2$ system is found to be 1.1. This fact suggests that the hydrogen storage capability of this $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy is superior to that of LaNi_5 system alloy.

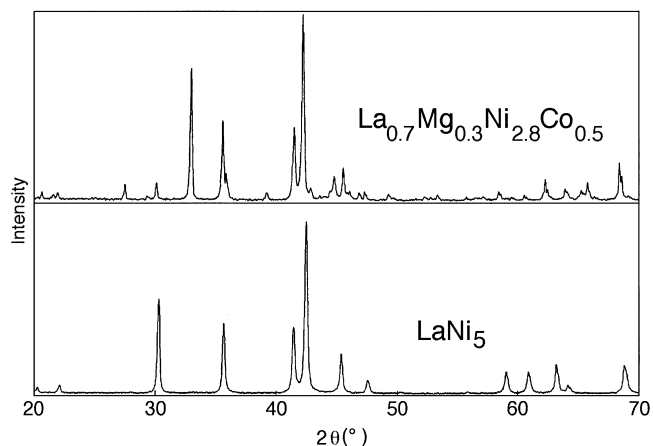


Fig. 2. X-ray diffraction patterns of $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy and LaNi_5 alloy.

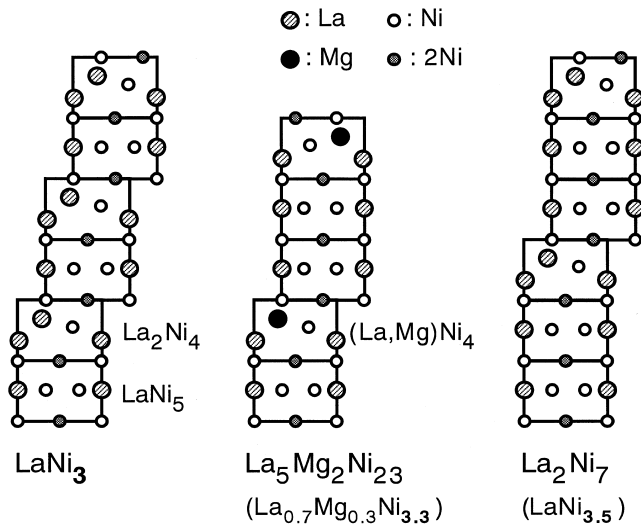


Fig. 3. The structure model of $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy.

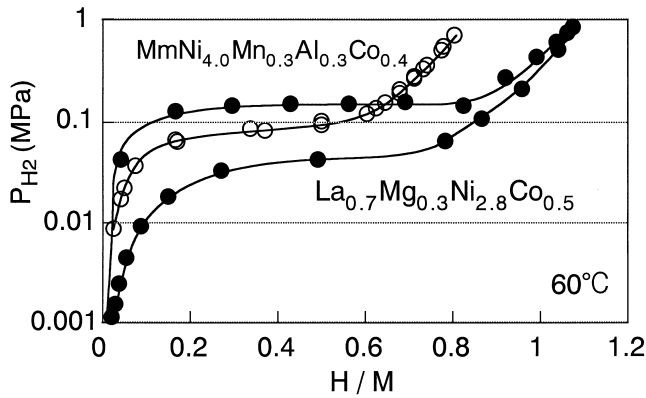


Fig. 4. P–C–T curves of $\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy and LaNi_5 system alloy.

4. Summary

$\text{La}_5\text{Mg}_2\text{Ni}_{23}$ system alloy ($\text{La}_{0.7}\text{Mg}_{0.3}\text{Ni}_{2.8}\text{Co}_{0.5}$) composed of stacked AB_5 and AB_2 structure subunits shows notably greater capacity up to 410 mAh/g in alkaline solution at room temperature than does LaNi_5 system alloy. This alloy electrode was an effective means to improve the charge–discharge capability of the negative electrode. These results suggest the possibility of realizing a lightweight battery with higher capacity than those employing alloys commonly adopted at present.

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