



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Surface treatment of rare earth-magnesium–nickel based hydrogen storage alloy with lithium hydroxide aqueous solution

Huiping Yuan^{*}, Kang Yang, Lijun Jiang, Xiaopeng Liu, Shumao Wang

General Research Institute for Nonferrous Metals, Beijing 100088, China

ARTICLE INFO

Article history:

Received 10 October 2014

Received in revised form

27 January 2015

Accepted 29 January 2015

Available online 28 February 2015

Keywords:

Rare earth-magnesium–nickel based

Hydrogen storage alloy

Surface treatment

Lithium hydroxide

Electrochemical character

ABSTRACT

The alkaline treatments of rare earth-magnesium–nickel based hydrogen storage alloy with lithium hydroxide (LiOH) aqueous solutions of various concentrations (1 M, 2 M, 4 M, 5 M, and 6 M) were investigated. The morphology and composition of the alloy surface and the electrochemical characters of the electrode were tested. The discharge capacity and cycle life of the alloy electrode were effectively improved after the treatment with LiOH solution of 5 M or higher. The samples treated in 5 M LiOH for 1 h and 6 M LiOH for 10 min showed better electrochemical properties than the other samples. The passive oxide and hydroxide layer formed in LiOH solution increased the charge retention rate and decreased the high rate dischargeability of the alloy electrode. The high concentration LiOH solution diminished the formation of oxygen containing species on the alloy surface during the treatment. The LiOH solution can remove the Mg element on the alloy surface effectively. Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Hydrogen storage alloy used as the negative electrode of nickel-metal hydride (Ni-MH) battery is required to be of good electrocatalytic activity, anti-corrosion in alkaline electrolyte, and cyclic durability. Its performances are not only depended on the alloy composition but also on the surface state [1–3]. Alkaline treatment is an effective method for improving the electrochemical properties of metal hydride electrodes [4–11]. It was reported in previous studies that the high rate dischargeability, cycle life, and charge efficiency were improved after the treatment in alkaline solutions. The Ni rich sub-layer

formed during the alkaline treatment accelerated the H absorption on the alloy surface [4,5].

The surface of the hydrogen storage alloy is oxidized easily in the alkaline solution. The oxide layer affects the electrocatalytic activity seriously. Therefore, the reduced agents, such as H_3PO_4 , $NaBH_4$, and KBH_4 , were added in the alkaline solutions [6–11]. They can enhance the etching effect of the alkaline treatment and reduce the surface oxidation of the alloy powders. It was also found that the H absorption was accelerated even after the significant oxidation [12,13]. Auger electron spectroscopy (AES) results showed that the alkaline atoms in the surface oxide layers could reduce the work function for the electrons of the alloy powders and help the

^{*} Corresponding author.

E-mail address: huiping.yuan1@gmail.com (H. Yuan).
<http://dx.doi.org/10.1016/j.ijhydene.2015.01.167>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

transportation of the electrons from the alloy surfaces to the H_2 and H_2O molecules [14,15].

However, there are also some disadvantages of the alkaline treatments. The repeating hydrogenation and dehydrogenation during the alkaline treatment cause the surface micro-cracks and the pulverization of the alloy powders. The smaller the initial grain size was, the faster the pulverization rate was [5]. It was also found the charge retention rate decreased after the alkaline treatment [8].

The previous studies of the alkaline treatments mostly focused on AB_5 -type alloys. Their low power characteristics and capacities limit the application of Ni-MH batteries. Recently, $AB_{3-3.8}$ -type rare earth-Mg-Ni based alloys with higher hydrogen storage capacities and fine electrochemical properties have been developed as the alternatives. However, their pulverization and corrosion rates in alkaline electrolyte are faster than AB_5 -type alloys. It was proved the nickel, cobalt, or copper coating enhanced the catalytic activity, the maximum discharge capacity, and the cyclic stability of the rare earth-Mg-Ni based alloy electrodes [16–19]. The KOH solution containing KBH_4 can also improve the cycle life of $La_{0.7}Mg_{0.3}Ni_{2.4}Co_{0.6}$ hydrogen storage alloy [11]. Recently, Nakatsuji et al. have invented a new method for treating the rare earth-Mg-Ni based hydrogen storage alloy with LiOH solution. This method can effectively remove the oxide and hydroxide precipitations on the alloy surface [20]. It has also been reported that the existence of Li atoms in the surface oxide layer can accelerate the H_2 dissociation and the H permeation through the oxide layer [21]. The effect of LiOH solution on the rare earth-Mg-Ni based hydrogen storage alloy was better than that of KOH and NaOH solutions.

In this work, the effect of LiOH aqueous solution on the $(REMg)_2(NiAl)_7$ hydrogen storage alloy was investigated. To improve the cyclic stability, the charge retention rate, and other electrochemical properties, the alkaline treatments in LiOH solutions of various concentrations were carried out. The morphologies and electrochemical properties of the $(REMg)_2(NiAl)_7$ hydrogen storage alloys were tested before and after the treatment.

Experimental

The commercial $(REMg)_2(NiAl)_7$ hydrogen storage alloy powders with A_2B_7 -type crystal structure of more than 90 wt% and a small amount of AB_3 , AB_5 , and A_5B_{19} phases were used. The alloy powders were obtained from Xiamen Tungsten Co., Ltd. To investigate the effect of alkaline treatment, the alloy powders were immersed in LiOH aqueous solutions at 363 K under mechanical stirring. The concentrations of LiOH aqueous solutions were 1 M, 2 M, 4 M, 5 M, and 6 M. The immersing times were 10 min, 20 min, and 60 min. After the completion of this step, the mixture was allowed to stand to settle the hydrogen storage alloy powders and the supernatant LiOH solution was removed. Then, the alloy powder was washed with distilled water and dried in vacuum at 333 K.

The metal hydride electrode was made by mixing 200 mg pure alloy powder with 800 mg Ni powder and cold pressing the mixture into a pellet of 16 mm in diameter under 530 MPa pressure. The alloy pellet was sandwiched between two

foamed Ni plates (60 mm × 20 mm) with a Ni wire soldered on to form a negative electrode. Electrochemical measurements were carried out in a half-cell consisting of metal hydride electrode as the working electrode, sintered $Ni(OH)_2/NiOOH$ as the counter electrode, and 6 M KOH solution as the electrolyte at 298 K. The working electrodes were charged at 60 mA g^{-1} for 7.5 h followed by a 10 min rest and discharged at 60 mA g^{-1} to the cut off potential of -1.0 V . High rate dischargeability (HRD) was described as $C_i/C_{max} \times 100\%$, where C_i was the discharge capacity at the discharge current density $i \text{ mA g}^{-1}$ and C_{max} denoted maximum discharge capacity at 60 mA g^{-1} . Charge and discharge current density of 300 mA g^{-1} were conducted to test the cycle lives of the metal hydride electrodes after the activation of 10 cycles.

The surface morphology of the alloy powder was observed using scanning electron microscopy (SEM) with a Hitachi-S4800 Unit operating at 10 kV. The surface state and the element distribution of the alloy powder were examined by auger electron spectroscopy (AES). AES depth profiles were measured using a PHI-700 scanning auger nanoprobe with an electron beam of 5 kV and 5 nA. The samples were sputtered with Ar^+ on an area of $2 \text{ mm} \times 2 \text{ mm}$ at 3 kV and $2 \mu\text{A}$. The oxygen content of the alloy powder was determined by the pulse heating inert gas fusion-infrared absorption method. The magnetization was tested by vibrating sample magnetometer (VSM).

Results and discussion

Surface and microstructure characteristics

Fig. 1 shows the morphologies of the $(REMg)_2(NiAl)_7$ hydrogen storage alloys treated in LiOH aqueous solutions with the concentrations of 2 M, 4 M, 5 M, and 6 M. It is obvious that the alloy surfaces were covered with rod-like and needle-like precipitates. With the increase of the LiOH concentration, the amount of rod-like and needle-like products on the alloy surface increased. When the concentration reached to 6 M, the column-shaped things appeared. During the treating process, some elements dissolved in the alkaline solution, such as Mg ion, light rare-earth metal ions, and complex anions. The hydroxides of the dissolved metals in the solution increased gradually and re-precipitated on the surface of the alloy powder. With the accumulation of the hydroxides, the dissolving speeds of the metal elements went down sharply. The hydroxides served as the barrier for further corrosion [9]. The porous surfaces formed by the corrosion and etching of the alkaline solution are rich in Ni atoms that can improve the reaction activity and raise the oxidation resistance of the alloy electrodes [10].

Fig. 2 shows the energy dispersive spectrometer (EDS) analyses of O contents on the $(REMg)_2(NiAl)_7$ alloy surfaces after treated in LiOH solutions of various concentrations. It can be seen from this figure the O content first increases and then decreases with the LiOH concentration for the same treating time. When the alloy powders were treated in 6 M LiOH solution for 10 min and 20 min and in 5 M LiOH solution for 60 min, the O content reversed to decrease. This suggests that the high concentration of 6 M or lower concentration of 5 M with longer treating time can help diminish the oxygen content on the alloy powder. The O contents were also tested

Download English Version:

<https://daneshyari.com/en/article/7715975>

Download Persian Version:

<https://daneshyari.com/article/7715975>

[Daneshyari.com](https://daneshyari.com)