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Journal of Alloys and Compounds 414 (2006) 207–214

Journal of ALLOYS AND COMPOUNDS

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Effect of a magnesium depletion on the Mg–Ni–Y alloy hydrogen absorption properties

Masanori Hara *, Shotaro Morozumi, Kuniaki Watanabe

Hydrogen Isotope Research Center, Toyama University, Gofuku 3190, Toyama 930-8555, Japan

Received 8 December 2004; received in revised form 28 February 2005; accepted 9 May 2005
Available online 24 August 2005

Abstract

To improve the hydrogen absorption properties of Mg_2Ni, three kinds of specimens were prepared. They were denoted as MGNIY, DeMg–MGNIY and DeMg–MIX. The first one was a cast Mg–Ni–Y alloy, the second was prepared by vacuum heating of MGNIY to remove some part of Mg and the third was prepared by vacuum heating of a mixture of pulverized Mg–Y and Mg_2Ni. The term DeMg denotes removal of Mg by vacuum heating. These samples were characterized by XRD, SEM and EPMA and found to be composed of Mg, Mg_2Ni and crystallographically unknown phases. Each material was found to have its own distribution of yttrium. The composition of the crystallographically unknown phase was determined by EPMA to be $MgYNi_3$. Yttrium-alloying and subsequent DeMg treatment caused a significant improvement in the hydrogen absorption rate. It showed hydrogen uptake amounting to about 3 mass% for DeMg–MGNIY at 473 K in 80 ks, although the improvement at room temperature could not be distinguished from that of Mg_2Ni. MGNIY gave similar absorption properties with those of DeMg–MGNIY at 473 K, but showed significantly slower absorption rate than Mg_2Ni at room temperature. The properties of DeMg–MIX were found to be similar to those of Mg_2Ni at both temperatures. On account of the sample characterization, it was concluded that the improvement in hydrogen uptake by DeMg–MGNIY and MGNIY at 473 K was due to their specific yttrium-distribution and catalytic activity.

Keywords: Mg-based alloys; Hydrogen absorption; Magnesium depletion; Mg_2Ni; Yttrium-alloying

1. Introduction

Extensive attention has been paid to the utilization of magnesium-based alloys as hydrogen storage materials owing to their high storage capacity [1,2] and low specific weight. Among them, Mg_2Ni is considered to be one of the most promising materials because of its favorable thermodynamic properties [3] to form adequately stable hydride at moderate temperatures. Its activation, however, is not easy and the hydrogen absorption rate is too slow at the temperatures of interest to practical applications [2]. To improve these properties, a number of investigations have been carried out and shown that the addition of rare earth elements to Mg_2Ni effectively speeds up the absorption rate [4–8]. Both melt-and-cast processing as well as mechanical alloying [9–12] are applicable for this purpose, but the latter is more effective for an enhancement of the rate of hydrogen absorption.

From the viewpoint of industrial production, the melt-and-cast method appears to be more appropriate than mechanical alloying because of its simplicity. The present authors have reported that a removal of Mg from Mg-containing hydrogen storage materials including Mg_2Ni by evaporation can improve the hydrogen absorption rate. They found that this is partly due to the formation of a porous structure to enlarge the specific surface area [13] and partly owing to not well-understood effects arising from the evaporation [14]. To examine the combination of yttrium-alloying to Mg_2Ni and removal of Mg from prepared alloys or compounds by vacuum heating, three kinds of specimens were prepared. They were denoted as MGNIY, DeMg–MGNIY

* Corresponding author. Tel.: +81 76 445 6922; fax: +81 76 445 6931.
E-mail address: hara@hrc.toyama-u.ac.jp (M. Hara).

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doi:10.1016/j.jallcom.2005.05.048

and DeMg–MIX. MGNIY was as-cast Mg–Ni–Y, which was prepared from Mg, Ni and Y by means of a melt-and-cast method. DeMg–MGNIY was obtained by vacuum heating of MGNIY via removal of Mg. This method was called "magnesium depletion treatment" and denoted by DeMg in this paper. DeMg–MIX was prepared by vacuum heating of a mixture of pulverized Mg–Y and Mg_2Ni. The effectiveness of yttrium addition and/or evaporation removal of Mg was examined by the rate and the extent of hydrogen absorption along with sample characterization by means of XRD, SEM and EPMA.

2. Experimental

2.1. Sample preparation and characterization

Three kinds of samples denoted as MGNIY, DeMg–MGNIY and DeMg–MIX were prepared as follows.

As-cast MGNIY was prepared following a conventional industrial flux process in small scale, i.e. 6.5 g of Mg were melted at 1073 K by a flux procedure and then 0.5 g of yttrium was added. After stirring for 30 min, 3.0 g of Ni was added to the solution at 1123 K, and stirring continued for 60 min. According to X-ray fluorescence analysis with a Philips PW23000 spectrometer equipped with UniQuant 3.0 program, the composition of MGNIY was 65.1%Mg, 30.2%Ni and 4.5%Y by weight.

To prepare DeMg–MGNIY, a 10 mm × 10 mm × 10 mm cube of MGNIY was cut from an ingot. The cube was placed in a vacuum apparatus, where it was heated rapidly up to 873 K and evacuated at this temperature for a period of 4 h in vacuum below 1×10^{-3} Pa. Vacuum heating caused the sample weight to decrease from 2.703 to 2.330 g along with a change in the sample shape, i.e. the corners of the cube became roundish and the centers of the planes dimpled to form a discus with concaved faces. Under the assumption that the weight loss is due to evaporation of Mg, the composition of DeMg–MGNIY was estimated to be 60%Mg, 35%Ni and 6%Y by weight.

DeMg–MIX was prepared from Mg_2Ni and 88%Mg–12%Y ingots separately pulverized to 100 mesh, by mixing 1.2 g of the former and 0.8 g of the latter. From the mixture, a compacted disc of 10 mm diameter and 4 mm thickness was prepared by applying 150 MPa for 1 min under air and room temperature. Vacuum heating of the disc at 873 K for 1 h caused a weight reduction from 0.853 to 0.658 g, from which the composition of DeMg–MIX was estimated to be 52%Mg, 42%Ni and 6%Y by weight. In addition to the above mentioned specimens, a commercial Mg_2Ni powder (below 100 mesh) of Kohjundo Kagaku Co. was also used as reference material.

Samples were characterized with an X-ray diffractometer using Cu Kα rays and an electron probe X-ray microanalyzer (EPMA).

2.2. Hydrogen absorption measurements

A constant-volume method was applied to measure hydrogen absorption curves. To avoid surface poisoning by impurity gases, a high vacuum system was used. The system was equipped with a vessel of known volume, a pressure gauge for up to 2 MPa, a stainless steel reaction cell of 6.4 mm diameter and 280 mm length provided with a valve, a vacuum gauge and gas supply lines.

The system was evacuated with a turbo-molecular pump backed by an oil-sealed rotary pump and its residual pressure was routinely below 1×10^{-4} Pa. Each sample was pulverized to powder of approximately 70 mesh and 0.141 g of the powder was introduced into the sample tube. High purity hydrogen from Nihon Sanso Co. was used without further purification.

The sample powder was activated by vacuum heating at 573 K for 2 h with an electric furnace. Temperatures were measured with a thermocouple placed on the outer surface of the reaction cell. Subsequently, the sample was cooled down to a given temperature and 2.5 mmol of hydrogen gas introduced into the reaction cell. The pressure change with time by hydrogen absorption was registered

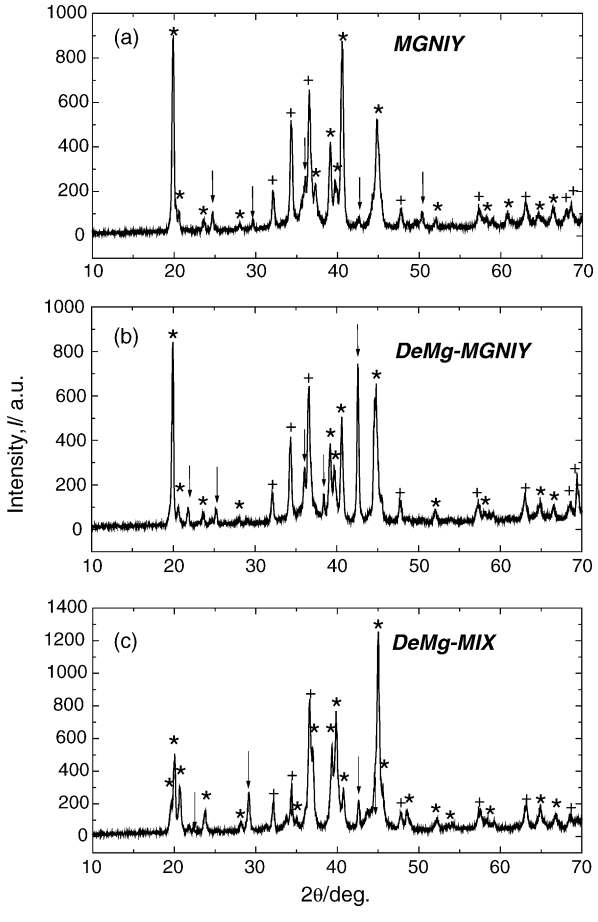

Fig. 1. X-ray diffraction patterns of the prepared materials MGNIY, DeMg–MGNIY and DeMg–MIX. "*" and "+" mean Mg_2Ni and Mg peaks, respectively. Arrows indicate unidentified peaks.