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Effects of annealing and stoichiometry to (Nd, Mg)(Ni, Al)$_{3.5}$ metal hydride alloys

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HIGHLIGHTS

- The influences of stoichiometry and annealing to Nd-A2B7 alloys were studied.
- Secondary phases are critical as catalyst for hydrogen storage.
- Annealing improves capacity and high-rate dischargeability.
- Annealed AB3.5 has the best electrochemical properties.

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ABSTRACT

The structures, gaseous phase hydrogen storage, and electrochemical properties of a series of $(Nd_{0.83}Mg_{0.16}Zr_{0.01})(Ni_{0.953}Al_{0.046}Co_{0.001})_{\alpha}$ alloys, where α = 3.3, 3.4, 3.5, 3.6, and 3.7, before and after annealing (900 °C and 5 h in argon) were studied. Besides the main Nd_2Ni_7 phase, other secondary phases, such as $MgNdNi_4$, $NdNi_5$, $NdNi_3$, NdNi, and $CeNi_3$, were present in most of the samples and influenced the hydrogen storage properties. After annealing, several changes happened: the stoichiometry of the main Nd_2Ni_7 phase remained constant at B/A = 3.3 and its abundance increased; the abundances of the major secondary phases decreased but were not totally eliminated (which helped preserve the catalytic effects); both the gaseous phase hydrogen storage and electrochemical capacity increased; the high-rate dischargeability decreased slightly; and the activation became more difficult. A stoichiometry of AB3.5 showed the best compromise among electrochemical capacity, high-rate dischargeability, and ease of activation.

1. Introduction

Rare earth (RE) magnesium-based AB_3- or A_2B_7-types of metal hydride (MH) alloys are promising candidates to replace the currently used AB_5 MH alloys as the negative electrodes in nickel/metal hydride (Ni/MH) batteries due to their high capacities and good high-rate dischargeability (HRD) [1]. The structures of AB_3- ($CeNi_3$ or $PuNi_3$) and A_2B_7-types (Ce_2Ni_7 or Gd_2Ni_7) are similar [2], being composed of alternating A_2B_4 (Laves-type) and AB_5 construction blocks [3,4]. Other similar A_2B_4/AB_5 mixed structures, such as Pr_5Co_{19} and Ce_5Co_{19} [5–13], were also proposed as MH alloys. While most of the RE-Mg–Ni MH alloys were based on La-only cases [4,14–23], other RE metals in misch-metal form were also considered [24–26]. Nd is an RE element with lower chemical activity compared to La and can be used to increase the oxidation resistance and extend the cycle life of the RE–Mg–Ni MH alloys. Mixed (La, Nd)–Mg–Ni alloys were studied, and a small amount of Nd (10% of A-site) was shown to increase both the surface exchange current and bulk diffusion and thus improve the HRD [27,28], cycle stability [29,30], and discharge capacity [31]. Another study in low-Co (La, Nd)–Mg–Ni alloys showed that 50% of Nd in A-site gave the best combination of capacity, HRD, and cycle stability [32].

Studies on Nd as the only RE element in RE–Mg–Ni MH alloys have been conducted before. A series of $Nd_{0.75}Mg_{0.25}(Ni_{0.8}Co_{0.2})_{\alpha}$ alloys, where α = 3.5 [33], 3.8 [34], and 4.5 [34], was studied. The sample with $AB_{3.5}$ stoichiometry showed the highest electrochemical capacity and HRD. While comparing the different preparation methods of the same $Nd_{0.75}Mg_{0.25}(Ni_{0.8}Co_{0.2})_{3.5}$ alloy, the thermal annealing at 900 °C yielded the highest discharge capacity [33]; the magnetic annealing at 650 °C showed the best HRD [35]; and the quick quench by melt-spinning promoted the most stable cycle performance [36]. In a study of annealed $Nd_{0.88}Mg_{0.12}Ni_{3.10+x}Al_{0.20}$ (x = 0.0, 0.1, 0.2, 0.3) alloy, a stoichiometry of $AB_{3.5}$ showed the best charge retention and cycle stability [37]. Although the electrochemical properties of

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Mg–Nd–Ni based A_2B_7 were studied before, the contributions from annealing and secondary phases were not discussed. Therefore, both the annealing and stoichiometry of a series of Nd-based A_2B_7 alloys are examined in detail and reported in this study.

2. Experimental setup

Ingots were prepared in a 2-kg induction furnace from raw materials in elemental form (except for Mg, where $MgNi_2$ was used to suppress the evaporation of Mg) under 1 atm of helium. Extra amount of Mg was added to compensate the losses during melting and annealing. The ingot was annealed at 900 °C for 5 h in 1 atm of argon. The annealing conditions were optimized by the electrochemical properties with the same methodology used in the annealing experiment on the mish-metal based A_2B_7 alloys reported previously [38]. The chemical composition of each sample was examined by a Varian *Liberty* 100 inductively-coupled plasma (ICP) system. A Philips *X'Pert Pro* x-ray diffractometer (XRD) was used to study the microstructure, and a JOEL-*JSM6320F* scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) capability was used to study the phase distribution and composition. PCT characteristics for each sample were measured using a Suzuki-Shokan multi-channel PCT system. In the PCT analysis, each sample was first activated by a 2-h thermal cycle between 300 °C and room temperature at 25 atm H_2 pressure. The PCT isotherms at 30, 45, and 60 °C were then measured.

For the electrochemical study, the ingot was first ground and then passed through a 200-mesh sieve. The sieved powder was then compacted onto an expanded nickel metal substrate by a 10-ton press to form a test electrode (about 1 cm^2 in area and 0.2 mm thick) without using any binder. Discharge capacities of these small-sized electrodes were measured in a flooded-cell configuration using a partially pre-charged $Ni(OH)_2$ pasted electrode as the positive electrode and a 6 M KOH solution as the electrolyte. The system was charged at a current density of 100 mA g^{-1} for 5 h and then discharged at a current density of 100 mA g^{-1} until a cut-off voltage of −0.9 V was reached. The system was then discharged at a current density of 24 mA g^{-1} until a cut-off voltage of −0.9 V was reached and finally discharged at a current density of 8 mA g^{-1} until a cut-off voltage of −0.9 V was reached. Linear polarization was performed by scanning the potential from −20 to +20 mV of the open circuit voltage at a rate of 0.1 mV s^{-1}. For the potentiostatic discharge experiment, electrode in a fully charged state was polarized +0.6 V vs. the open circuit voltage for 7200 s.

Table 1
Design compositions and ICP results in at.%.

Alloy		Nd	Zr	Mg	Ni	Co	Al	Fe	B/A
AB3.3	Design	19.3	0.2	3.7	73.1	0.1	3.5	0.0	3.30
	ICP as-cast	19.4	0.2	3.8	73.1	0.1	3.4	0.1	3.28
	ICP annealed	19.1	0.2	3.8	73.2	0.1	3.4	0.1	3.32
AB3.4	Design	18.9	0.2	3.6	73.7	0.1	3.5	0.0	3.41
	ICP as-cast	19.0	0.2	3.4	73.7	0.1	3.5	0.1	3.42
	ICP annealed	18.8	0.2	3.3	73.9	0.1	3.6	0.1	3.48
AB3.5	Design	18.4	0.2	3.6	74.1	0.1	3.5	0.0	3.50
	ICP as-cast	18.5	0.2	3.5	74.1	0.1	3.5	0.1	3.50
	ICP annealed	18.2	0.2	3.6	74.3	0.1	3.6	0.1	3.55
AB3.6	Design	18.0	0.2	3.5	74.6	0.1	3.5	0.0	3.60
	ICP as-cast	18.3	0.2	3.4	74.3	0.1	3.5	0.1	3.56
	ICP annealed	18.0	0.2	3.6	74.6	0.1	3.4	0.1	3.59
AB3.7	Design	17.7	0.2	3.4	75.0	0.1	3.6	0.0	3.70
	ICP as-cast	17.6	0.2	3.5	75.0	0.1	3.5	0.1	3.70
	ICP annealed	17.8	0.2	3.4	74.9	0.1	3.5	0.1	3.67

3. Results and discussion

Five alloys (ABα) with design formula $(Nd_{0.83}Mg_{0.16}Zr_{0.01})(Ni_{0.953}Al_{0.046}Co_{0.001})_\alpha$, where α = 3.3, 3.4, 3.5, 3.6, and 3.7, were prepared. ABαA denotes alloy after annealing. These alloys are similar to those reported in Ref. 37 with the addition of a very small amount of Zr to enhance the cycle life [39] and Co to facilitate activation [40]. The ICP results from ingots before and after annealing in atomic percentage are compared in Table 1, which are very close to the designed compositions shown in the same table

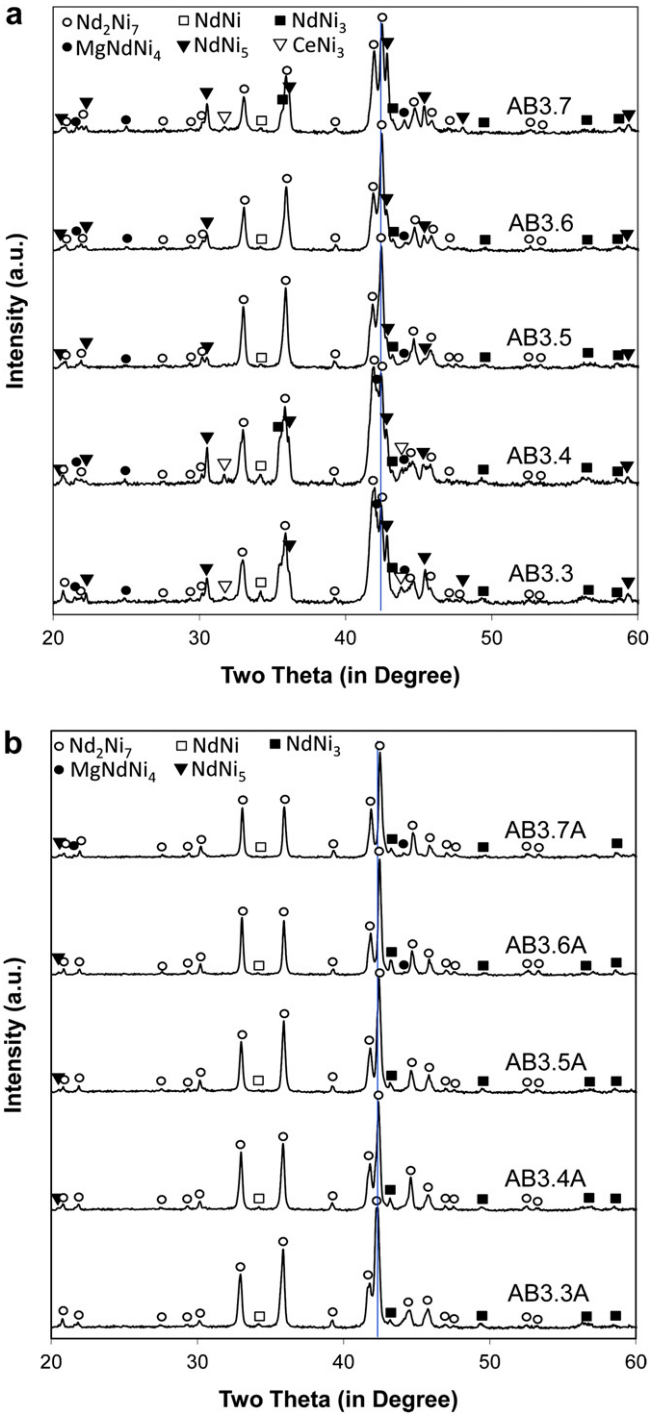

Fig. 1. XRD patterns using Cu-K_α as the radiation source for as-cast (a) and annealed (b) Samples.