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Influence of Ce and Nd contents of Ml(NiCoMnAl)$_5$ alloy on the performances of Ni–MH batteries

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Abstract

The influence of the Ce and Nd contents of Ml(NiCoMnAl)$_5$ alloy on the performances of Ni–MH batteries was studied. It was found that the high rate dischargeability increased with increase of the Ce content and decrease of the Nd content, while charge retention decreased. An increase in the Ce and Nd contents improved the Ni–MH battery cycle life, and increase of the Nd content increased the discharge capacity of the MH electrode. XRD and PCI analysis showed that heat treatment made the chemical composition of the hydrogen storage alloy more homogeneous with lower lattice strain, and the hydrogen desorption plateau was smooth, which obviously improved the Ni–MH battery cycle life.

Keywords: AB_5 alloy; Ce and Nd contents; Discharge capacity; Ni–MH battery; Cycle life

1. Introduction

The hydrogen storage alloy powder used for the Ni–MH battery greatly affects the battery cycle life, the discharge capacity and the high rate discharge characteristics, so the hydrogen storage alloy powder is required to have higher discharge capacity, long cycle life, suitable hydride decomposition pressure, good electrochemical catalysis activity and anti-oxidation characteristics. At present, practical hydrogen storage materials are mainly divided into rare earth based AB_5 alloys and Ti(Zr) based alloys. The material cost, the low temperature and high rate discharge characteristics and the activity of AB_5 alloys are better than those of Ti(Zr) alloys, but the discharge capacity is low. There have been many investigations of the A composition of AB_5 alloys, however the cooperative effects of the Ce and Nd contents of AB_5 alloy on cycle life, discharge capacity, self-discharge and high rate discharge performance of Ni–MH batteries have been little studied. Sridhar [1] and Adzic [2] reported that the substitution of La and Ni, respectively, by Ce and Co could increase the MH electrode cycle life, but reduced the discharge capacity. Sakai [3,4] reported that increasing the Ce and Nd ratio to La of mischmetal improved MH electrode cycle life even if the Co content of the AB_5 alloy was low, and the discharge capacity was also reduced. Therefore, the mischmetal composition of the AB_5 alloy must be optimized. The cooperative effects of the Ce and Nd contents of the AB_5 alloy on the performances of Ni–MH batteries are investigated in this paper.

2. Experimental

Ml(NiCoMnAl)$_5$ alloys (Ml: La-rich mischmetal) were prepared using a vacuum induction melting furnace. The melt was poured into a water-cooled mold. The alloy ingots were mechanically pulverized. The alloy powders passed through a 200 mesh sieve with a mean diameter of 40–50 μm. Pressure–composition isotherms (PCI) were measured at 45°C with a computer-controlled Sieverts' apparatus. The Ce and Nd contents of the mischmetal are listed in Table 1. The La content is fixed.

The electrodes were made by mixing the hydrogen storage alloy powder with a conductive agent, binder and deionic water. A perforated metal ribbon was coated with

Table 1
Ce and Nd contents of the mischmetal

	Alloy No.					
	1	2	3	4	5	6
Ce (wt.%)	35	30	25	15	10	5
Nd (wt.%)	10	15	20	25	30	35

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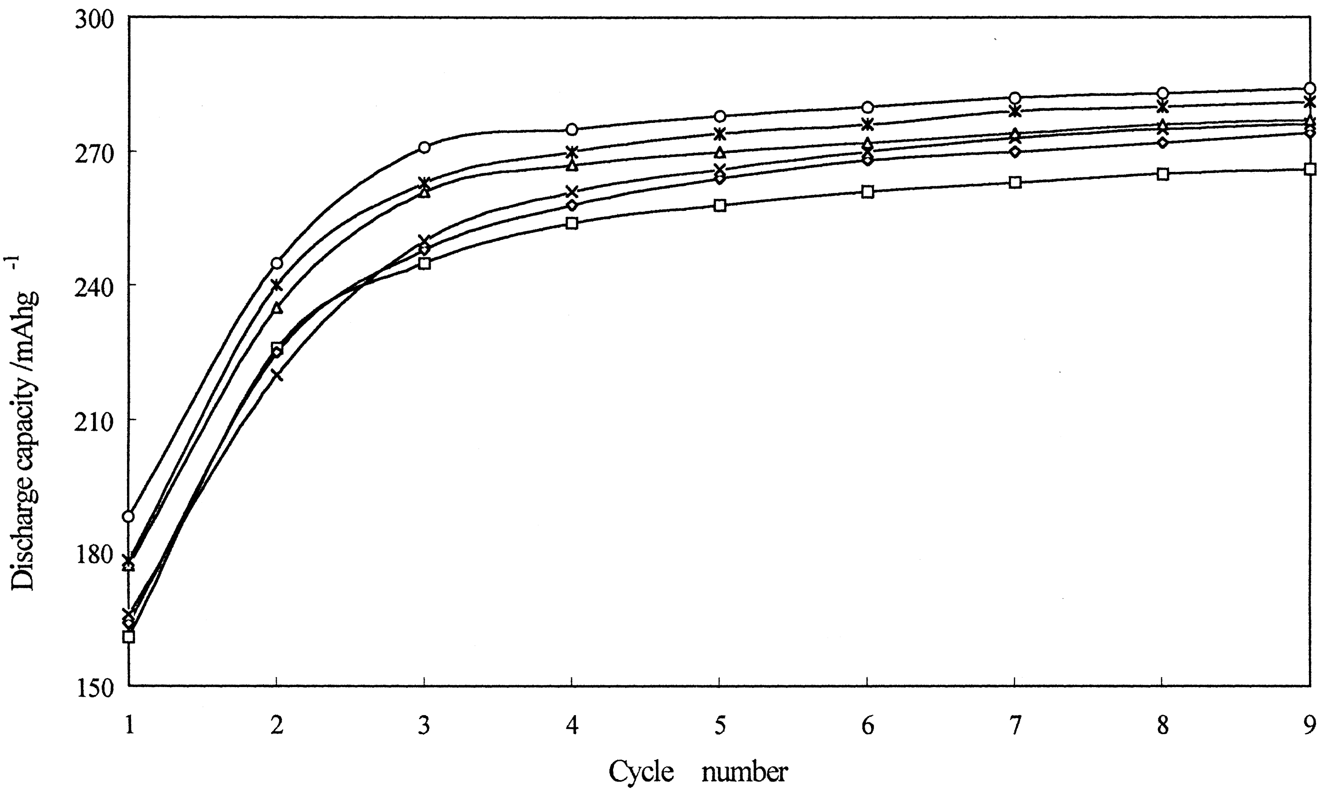

Fig. 1. Relationship of Ce and Nd contents to MH electrode discharge capacity: (□) alloy 1; (◊) 2; (×) 3; (△) 4; (*) 5; (○) 6.

this paste, then dried and pressed to an electrode of size 40×30×0.35 mm. The counter electrode was $Ni(OH)_2$/NiOOH. The reference electrode was Hg/HgO. The negative electrode was placed between a pair of positive electrodes, and separators were laid between the negative and positive electrodes, then clamped between two PVC sheets. The electrodes were charged for 7.5 h at 60 mA/g, and discharged to −740 mV vs. Hg/HgO at 60 mA/g.

AA size Ni–MH batteries were made using negative electrodes, positive electrodes, and KOH+LiOH aqueous solution as electrolyte. The nominal capacity of the battery was 1.2 Ah.

3. Results and discussion

3.1. Effect of the Ce and Nd contents of AB_5 alloy on MH electrode discharge capacity

Fig. 1 shows the relationship of the Ce and Nd contents of AB_5 alloy to the discharge capacities of MH electrodes. From alloys 1 to 6, their initial activity is similar. Discharge capacities stabilize after the fourth or fifth cycle. Discharge capacities increase with increasing Nd content and decreasing Ce content. According to a US patent [8], the MH electrode discharge capacity depends largely on the La and Pr contents of AB_5 alloy, and the effect of Ce and Nd contents is much less.

Table 2 shows that the unit cell volume decreases with increase of Ce and Nd contents, and the unit cell volume of $La_{1-x}Ce_xB_5$ alloy is smaller than that of $La_{1-x}Nd_xB_5$ alloy at the same molar ratio. This may cause a corresponding drop in the hydrogen absorption and desorption capacity.

3.2. Effect of Ce and Nd contents of AB_5 alloy on the high rate dischargeability of a Ni–MH battery

After activating, the discharge capacities of the AA batteries were tested at different discharge rates (1C, 3C

Table 2
Unit cell volumes of AB_5 alloy [2,5]

	x (molar ratio)							
	0.1	0.2	0.3	0.35	0.5	0.6	0.75	0.8
$La_{1-x}Ce_xB_5$ (Å^3)	–	88.84	–	88.16	87.33	–	86.19	–
$La_{1-x}Nd_xB_5$ (Å^3)	89.23	88.90	88.44	–	–	88.10	–	86.52

Table 3
Relationship of Ce and Nd contents to the high rate dischargeability of a Ni–MH battery

	Alloy No.					
	1	2	3	4	5	6
1C rate (%)	96.6	96.4	95.8	95.7	95.3	95.4
3C rate (%)	96.1	94.6	94.5	93.5	93.8	93.9
5C rate (%)	94.7	93.5	92.6	91.8	91.2	91.0

and 5C) with end-off voltage 1.0, 0.9 and 0.8 V, respectively. The charge condition was for 3.5 h at a rate of 0.4C. The ratios of the 1C, 3C and 5C rate discharge capacities to that of the 0.2C rate are listed in Table 3.

Increase of the Ce content of the AB_5 alloy improves the high rate dischargeability of the Ni–MH battery. The PCIs of alloys 1 to 6 are shown in Fig. 2. The hydride decomposition pressures gradually decrease from alloy 1 to 6. According to van t'Hoff's equation, the enthalpy ($-\Delta H$) for the formation of the metal hydride gradually increases from alloy 1 to alloy 6, with the stability of the hydrides in the reverse order, namely increasing from alloy 6 to alloy 1.

3.3. Effect of Ce and Nd contents of AB_5 alloy on Ni–MH battery self-discharge

After the AA type Ni–MH batteries were activated, they were charged for 3.5 h at a rate of 0.4C, and discharged to 1.0 V at a rate of 0.2C, as initial discharge capacities, then charged for 3.5 h at a rate of 0.4C and placed in an oven for 3 days at 45°C. The batteries were taken out and discharged to 1.0 V at a rate of 0.2C. The ratios of the discharge capacities to the initial capacities are shown in Table 4.

Table 4
Relationship of the Ce and Nd contents of AB_5 alloy to Ni–MH battery charge retention

	Alloy No.					
	1	2	3	4	5	6
Charge retention (%)	77.1	80.5	81.0	81.8	82.2	77.4

The battery charge retention increases with increasing Nd content from alloy 1 to alloy 5, but if the Nd content is too high, the charge retention decreaes noticeably.

Table 5
Relationship of Ce and Nd contents to Ni–MH battery cycle life

	Alloy No.					
	1	2	3	4	5	6
221st cycle capacity retention (%)	83.3	81.2	82.8	82.8	80.5	82.4

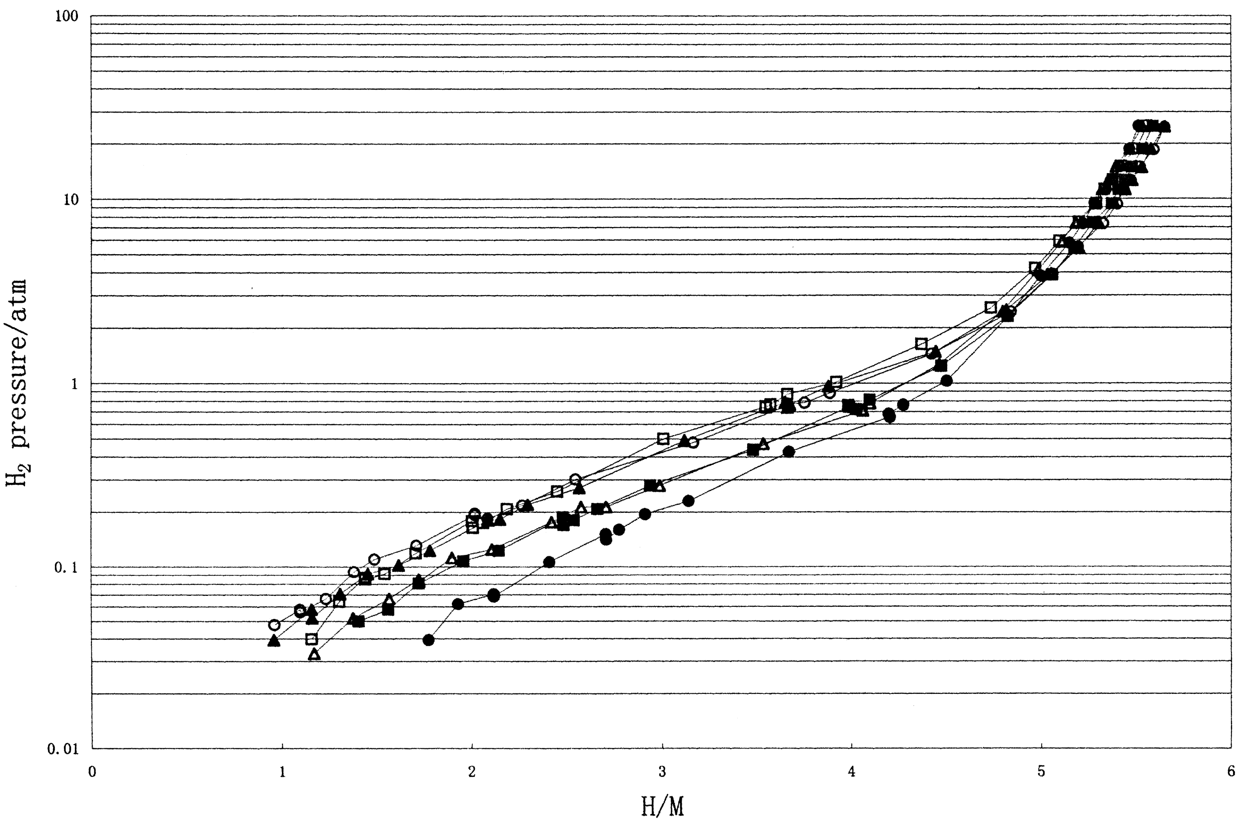

Fig. 2. PCIs of the hydrogen storage alloy: (▲) alloy 1; (□) 2; (○) 3; (△) 4; (■) 5; (●) 6.

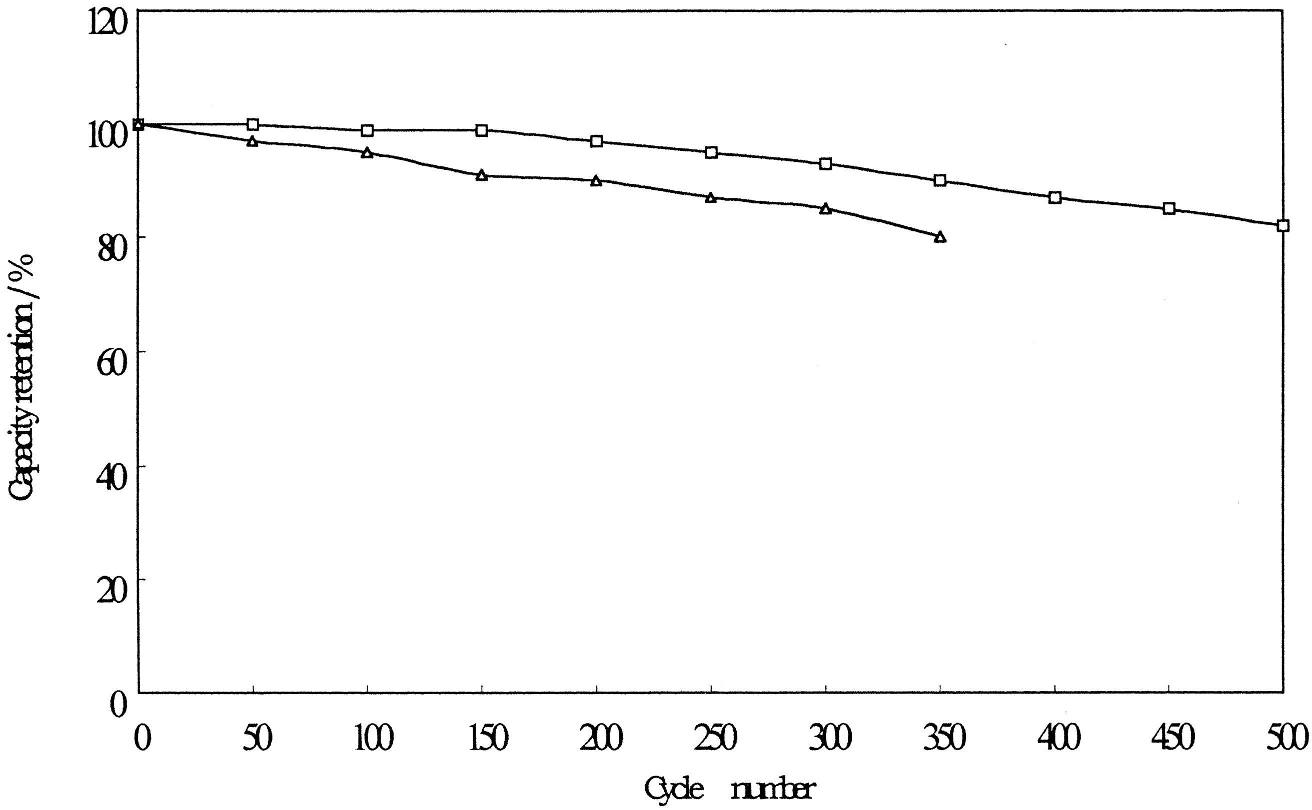

Fig. 3. Cycle curves af AB_5 alloy: (□) heat-treated alloy; (△) as-cast alloy.

3.4. Effect of Ce and Nd contents of AB_5 alloy on Ni–MH battery cycle life

Table 5 shows that an increase of the contents of both Ce and Nd improves the Ni–MH battery cycle life. Test method: batteries were charged for 72 min at 1200 mA, then discharged to 1.0 V at 1200 mA.

3.5. Effect of heat-treatment of hydrogen storage alloys on Ni–MH battery cycle life

An ingot of alloy 2 was annealed at 950–1100°C for 4–8 h, then mechanically pulverized to powder of <200 mesh. The batteries were manufactured using the same method described above. Cycle life test method: charging at 1200 mA, $-\Delta V = 10$ mV control, and then discharged to 1.0 V at 1200 mA. The results are shown in Fig. 3. Heat-treatment of hydrogen storage alloy markedly improves the Ni–MH cycle life, as reported previously [6,7,9].

XRD and PCI analyses show that the chemical composition of the heat-treated hydrogen storage alloy is more homogeneous, and the heat-treated hydrogen storage alloy has a lower lattice strain, which may improve the anti-pulverization and anti-corrosion characteristics of the alloy.

4. Conclusions

1. Increasing the Ce and Nd contents of $Ml(NiCoMnAl)_5$ alloy improves the Ni–MH battery cycle life, and increasing the Nd content increases the negative electrode capacity. Increasing the Ce content increases the battery self-discharge, but improves the high rate dischargeability of the Ni–MH battery.
2. Heat treatment of the hydrogen storage alloy makes the chemical composition more homogeneous, and it has a lower lattice strain, which obviously enhances the Ni–MH battery cycle life.

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