Non-stoichiometric Hydrogen Storage Alloys and Their Hydride Electrode Properties*

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Abstract: The phase structures, electrochemical properties and PCT characteristics of $MlNi_{3.55+x}Co_{0.75}Al_{0.3}Mn_{0.4}$ (Ml = Lanthanum-rich Michmetal, $0 \leqslant x \leqslant 0.6$) alloys have been investigated. The value of lattice constant a decreases, the value of lattice constant c and cell volume increase with the increasing value of x except for the alloy with $x = 0.6$. Increasing value of x facilitates segregation of Mn, Al elements, but does not obviously affect segregation of Ni element. The plateau pressures of PCT curve increases, the discharge capacities and cycling stability decrease slightly, but the activity is greatly improved with the increasing value of x.

Key words: hydrogen storage alloys; metal hydride electrode; rare earth metal; electrochemical properties; stoichiometry
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1 Introduction

Buschow et al[1] found that the stoichiometry significantly affected the hydrogen absorption-desorption properties of hydrogen storage alloy. Tadokoro et al[2] have studied the electrochemical characteristics of non-stoichiometric alloy $Mm(NiCoAlMn)_x$ ($x = 4.5 \sim 4.8$). It was found that non-stoichiometric alloy with boron added to form second phase had higher capacity and electrochemical reactivity than those of the stoichiometric alloy without boron added. Notten et al[3] found the AB_5-type B-rich alloy greatly improved the high-rate discharge capability. Notten et al[4,5] also studied the microstructure, PCT characteristics and charge-discharge cycling performance of $La(NiCu)_x$ and $LaNi_{x-1}Cu$ ($x = 5.0 \sim 6.0$) alloys. These studies were aimed at the development of Co-free alloys which would contribute to cost reduction. Notten found that the initial discharge capacity decreased and the cycling stability increased with the increasing stoichiometry x of the single-phase alloy. A model was proposed which could account for the cycling life behavior of these non-stoichiometric alloys. In general, AB_5-type non-stoichiometric alloy consists of two (or more) phases, among which the second phase with specific compositions is well distributed in main phase[6,7]. Non-stoichiometric alloy has excellent electrocatalysis, cycling stability and low-temperature discharge capability[6-11]. The effect of stoichiometry x on microstructures, electrochemical properties, PCT characteristics and thermodynamics property of the alloys $MlNi_{3.55+x}Co_{0.75}Al_{0.3}Mn_{0.4}$ ($0 \leqslant x \leqslant 0.6$) have been investigated in this paper.

2 Experimental

On the basis of our previous works[12], the values of the x of the alloys $MlNi_{3.55+x}Co_{0.75}Al_{0.3}Mn_{0.4}$ examined in this work are designed and listed in Tab.1. The Alloys were melted in a vacuum induction furnace under an argon atmosphere, and then were cooled by copper mould. The as-cast alloys were crushed and ground mechanically, then passed through a series of sieves. The fine powder with a size of less than 38 μm was used for X-ray powder diffraction (XRD) measurements. The powder with a size of 38 ~ 75 μm was used for electrochemical measurements.

Electrochemical properties of MH electrodes were tested in an half-cell (in 6 mol/L KOH electrolyte at 20 ℃ and 40 ℃) with a computer-controlled current source. The MH electrodes were fabricated by mixing the alloy powder (approximately 200 mg) with the fine copper in a mass ratio of 1:2, followed by cold pressing to a pellet ($d = 10$ mm, $p = 2.55 \times 10^9$ Pa). A $Ni(OH)_2$ electrode (sintered) with a larger capacity and a Hg/HgO (6 mol/L KOH) electrode were used as the counter-electrode and

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reference electrode respectively. Electrodes were charged at 0.2 c, 0.4 c and 1 c rate for 7.5 h, 3.5 h and 1.3 h, respectively, and discharged at the same rate to a cut-off potential of -0.600 V *vs* the Hg/HgO (6 mol/L KOH) electrode.

The microstructure analysis of the alloys was carried out using scanning electron microscopy (SEM). An electron probe microanalysis (EPMA) was undertaken to determine the composition. The phase structure and the lattice constants of the alloys were determined using X-ray diffraction (XRD).

P-C-T curves of the alloys were measured at 20 ℃ by electrochemical method. The enthalpy and entropy changes of hydrogen desorption were obtained via the Van't Hoff equation.

3 Results and discussion

3.1 XRD analyses

The XRD results indicated that all alloys examined in this work seemed to be single phase with the hexagonal $CaCu_5$-type crystal structure. The lattice constants (a, c) and cell volume of the alloys are summarized in Tab.1. It can be seen from Tab.1 that the value of lattice constant a decreases, the value of lattice constant c, c/a and cell volume increase with the increasing value of x except for the alloy with $x = 0.6$. For the B-rich alloys (in AB_5 alloys), some rare-earth atoms at the lattice point of the unit cell are replaced by two atoms of Ni in the shape of dumb-bell along c-axis direction, which makes lattice constant a decease and c increase[4]. Therefore, the value of c/a increases, which contributes to improvement of the charge-discharge cycling stability[13]. Their bigger lattice and cell volume are attributed to that there are some surplus atoms introduced into the unit cell in the non-stoichiometric alloys, which causes the cell expansion. But when $x = 0.6$, obvious segregation of the Side-B elements (see Tab. 2) makes the actual rich amount of Side-B atom decrease, which cause cell volume to increase.

Tab.1 Lattice parameters of the alloys $MlNi_{3.55+x}Co_{0.75}Al_{0.3}Mn_{0.4}$

x	Lattice constant		c/a	V(Cell)
	a/nm	c/nm		nm^3
0	0.50436	0.40318	0.7994	0.088820
0.2	0.50408	0.40440	0.8022	0.088991
0.4	0.50381	0.40595	0.8058	0.089236
0.6	0.50299	0.40405	0.8033	0.088529

Tab.2 The ratio of the element content in segregation spot and that designed(%) in the alloys $MlNi_{3.55+x}Co_{0.75}Al_{0.3}Mn_{0.4}$

x	La	Ni	Co	Mn	Al
0	107	96	95	95	145
0.2	118	86	92	190	181
0.6	5	72	144	406	268

3.2 Microstructure

From the characteristic X-ray images and the EPMA results it was found that the dendrite segregation existed in all alloys in various degrees. Microstructure was relatively homogeneous except obvious segregation of Mn in stoichiometric alloy($x = 0$) and serious segregation of Co, Mn, Al was observed in the non-stoichiometric alloy($x > 0$), especially for that of Co, Mn, Al (see Tab.2). But there was not obvious segregation of Ni in Tab.2, which is attributed to that Ni has stronger bond with rare earth metal than Co, Mn, Al have. SEM results shown that second phase existed inside dendrite or on the boundary of dendrite in all alloys.

3.3 Electrochemical properties

3.3.1 Discharge capacity and cycling stability

Fig. 1 shows the relationships between discharge capacity and cycle number for the alloys at 20 ℃. It can be seen from Fig. 1 that the discharge capacities and cycling stability decrease slightly, but the activity is greatly improved with the increasing value of x. The activity number reduces from 9 to 3 when x increase from 0 to 0.6.

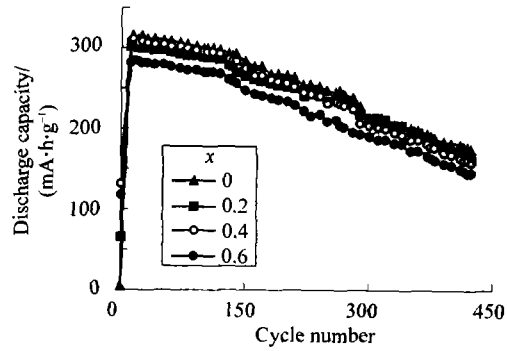

Fig.1 Discharge capacities *vs*. cycle number for the alloy electrodes
Charge current density: 0.4 c for 3.5 h;
Discharge current density: 0.4 c;
Cut off potential: -0.6 V *vs*. Hg/HgO

3.3.2 Discharge capacity at various temperatures

Discharge capacities at various temperatures at 0.2 c charge-discharge rate are listed in Tab.3. The discharge capacity at 40 ℃, compared with that at 20 ℃, only slightly decreased, and for all alloys the ratios were above

95%, which indicates that discharge capacity of the alloys studied in this work was hardly affected by temperature in the range of 20 ~ 40 ℃.

Tab.3 Discharge capacities under different charge-discharge conditions

x	0	0.2	0.4	0.6
20 ℃ 0.2 c capacity ($mA\cdot h\cdot g^{-1}$)	333.8	333.8	324.3	312.8
40 ℃ 0.2 c capacity ($mA\cdot h\cdot g^{-1}$)	329.7	327.5	315.7	297.8

An increase of temperature has two sides of effect on discharge capacity. An increase of temperature could generally make discharge capacity increase, but too much high temperature could make discharge capacity decrease, which have been explained in [12].

3.4 PCT Characteristics

PCT curves of the all alloys are showed in Fig.2. The midpoint pressure increased with the increasing x, which was consistent with the results of $LaNi_x$ ($x = 4.9 \sim 5.4$)[1] and $Mm(B_5)_x$ ($x = 0.88 \sim 1.12$)[8]. The reason is that the hydrogen pressure of metal hydride for Side-B elements is higher. The slope of the plateau decreased with the increasing stoichiometry x except for $x = 0.6$, which is attributed to obvious segregation of the Side-B elements for the alloy with $x = 0.6$.

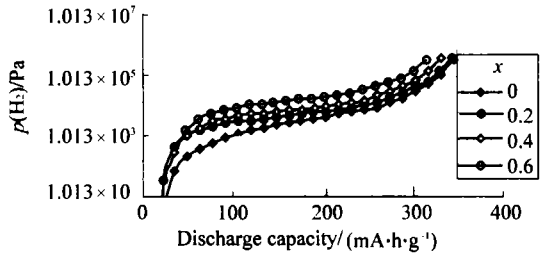

Fig.2 PCT curves of the four representative alloys

4 Conclusions

(1) The value of lattice constant a decreases, the value of lattice constant c and cell volume increase with the increasing value of x except for the alloy with $x = 0.6$ in $MlNi_{3.55+x}Co_{0.75}Al_{0.3}Mn_{0.4}$ ($0 \leqslant x \leqslant 0.6$) alloys.

(2) Increasing value of x facilitates segregation of Mn, Al elements, but does not obviously affect segregation of Ni element

(3) The plateau pressures of PCT curve increases, the discharge capacities and cycling stability decrease slightly, but the activity is greatly improved with the increasing value of x.

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非化学计量比贮氢合金及其电极特性

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摘 要: 对贮氢合金 $MlNi_{3.55+x}Co_{0.75}Al_{0.3}Mn_{0.4}$ ($0 \leqslant x \leqslant 0.6$) 的结构、组织、电化学性能和 $P-C-T$ 特性进行了研究。结果表明,除了 $x = 0.6$ 的合金外,随着 x 的增大合金的点阵常数 a 值减小、c 值增大,c/a 值和单胞体积也随之增大,而 $x = 0.6$ 时合金体积反而减小。同时随着 x 的增大,合金中 Ni 并没有出现明显偏析,而是促进了 B 侧其它合金元素尤其是 Mn 和 Al 的偏析。x 的增大,放电容量降低,充放电循环稳定性只略有下降,但活化性能却明显改善,$P-C-T$ 曲线平台压升高。

关键词: 贮氢合金;金属氢化物电极;稀有金属;电化学性能;化学计量比
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