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Electrochemical performance of Sn-substituted, $LaNi_5$-based rapidly solidified alloys☆

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Abstract

Sn-substituted, $LaNi_5$-based rapidly solidified alloys with low Co content, $La_{1-x}A_xNi_{4.25}Co_{0.5}Sn_{0.25}$(A=La, Nd, Ce, and x=0.2), were prepared by melt-spinning. The microstructure of the as-spun alloys was observed with SEM and the element distribution of the as-spun and annealed alloys was analyzed by EDX. It is found that the as-spun alloys had fine grains. However, there was Sn segregation in the grain boundaries of the as-spun alloys. XRD patterns show that for the as-spun alloys the lattice strain could be alleviated through vacuum annealing. The electrochemical performance of the as-spun and heat-treated alloys was investigated. It is found that the Ce-containing as-spun alloy had a cycle life more than 300 cycles. After heat-treatment, the electrochemical performance of the Ce-free alloys could be further improved, which is attributed to the alleviation of the lattice strain and the change of Sn distribution.

Keywords: Metal-hydride electrodes; Rare earth intermetallic compounds; AB_5 type hydrogen storage alloys; Melt spinning

1. Introduction

It is generally thought that Co is indispensable to AB_5 type hydrogen storage alloys at present because Co can restrain the pulverization and corrosion of the alloys in charge–discharge process.

However, this expensive metal increases the cost of the alloys at the same time. The results of lowering the alloy cost through substituting Co with such elements as Sn, Cu, Si have been reported in more than one article [1–5]. It can be seen from these results that Sn can decrease the equilibrium plateau pressure, improve the kinetics and the cycle life of the alloys. In this study, three Sn-substituted, $LaNi_5$-based rapidly solidified alloys with low Co content (6.3wt.%), $La_{1-x}A_xNi_{4.25}Co_{0.5}Sn_{0.25}$(A=La, Nd, Ce, and x=0.2), were prepared by melt-spinning. The electrochemical performance of the as-spun and annealed alloys was investigated in order to find a way to lower the cost of rare earth-nickel alloys.

2. Experimental details

As-cast $La_{1-x}A_xNi_{4.25}Co_{0.5}Sn_{0.25}$ alloys were prepared by melting the constituent elements (purity above 99%) in a 25 kg capacity vacuum induction melting furnace. The ingot was crushed into coarse particles, remelted and then rapidly solidified into thin ribbons in a 5T Advanced Melt Spinner made by Marko Materials, Inc., USA. The three kinds of alloys, $LaNi_{4.25}Co_{0.5}Sn_{0.25}$, $La_{0.8}Nd_{0.2}Ni_{4.25}Co_{0.5}Sn_{0.25}$ and $La_{0.8}Ce_{0.2}Ni_{4.25}Co_{0.5}Sn_{0.25}$, are briefly named as QAB_5-1, QAB_5-2 and QAB_5-3, respectively in the text. One part of each kind of ribbons was heat-treated in vacuum at 773 K and 973 K, respectively. The annealed ribbons were finally milled into powders below 200 mesh. The other part was milled into powders below 200 mesh directly.

XRD analysis was conducted in a Rigaku D/max-γ_A type X-ray diffractometer.SEM observation and EDX analyses were performed at an S-360 type SEM made by Cambridge Instrument Ltd.

The electrochemical performance was determined at BT-2043 battery testing system made by Arbin Company, USA. The process of sample preparation was made as the following:

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(a) Prepared total weight of 3.0000 g powders of hydrogen storage alloy and Ni with the ratio of 1:3;
(b) The powders were cold-pressed into a 25 mm diameter electrode disc at a pressure of 624 MPa;
(c) The disc was clamped between two NiOOH/Ni(OH)2 electrodes with excessive capacity and put into a beaker with 6M KOH solution.

The discharge capacity measurement was conducted at 298±1 K, The sample was charged at a current density of 60 mA/g for 8 h, rested for 5 min, and then discharged at the same current density to a cut-off voltage of 1V.

The charge–discharge cycle life was measured after the sample was activated for 10 cycles at a charge–discharge current density of 60 mA/g. The sample was charged for 1.75 h at a charge current density of 120 mA/g and discharged for 1.25 h at the same current density. A full charge–discharge was conducted every 30 cycles in the following way: the sample was charged for 3.5 h at a current density of 120 mA/g, rested for 0.5 h, and then discharged at 60 mA/g to a cut-off voltage of 1 V.

After the sample was activated for 10 cycles at a charge–discharge current density of 60 mA/g, the high-rate dischargeability (HRDA) was determined by the following equation

$$\mathrm{HRDA}(\%) = \frac{C_{600}}{C_{600} + C_{60}} \times 100$$

where C_{600} is the discharge capacity at 600 mA/g, C_{60} is the residual discharge capacity determined at *60* mA/g by resting 10 min after the measurement of C_{600}.

3. Results and discussion

3.1. The microstructure of the rapidly solidified alloys

The SEM images of the as-spun QAB_5-3 ribbons are shown in Fig. 1, which is representative of the microstructure of the three kinds of as-spun ribbons. It is shown that the as-spun alloys had very fine grains. Fracture observation showed that there were some columnar grains on the side touching the cooling wheel. From EDX analysis results listed in Table 1. It is found that there was Sn segregation in the grain boundaries of the as-spun alloys. And after annealing, there was a higher Sn content in grains than in grain boundaries. XRD patterns (Fig. 2) show that after annealing, some of the peaks became narrower and sharper, which indicates that the lattice strain was alleviated.

3.2. Electrochemical performance of the as-spun and heat-treated alloys

Figs. 3–5 show the relationship between the discharge capacity and the charge–discharge cycle of the as-spun and heat-treated alloys. The capacity retention ability after 300 charge–discharge cycles is listed in Table 2. It is found from these results that the as-spun alloys had low initial capacity and needed a little more charge–discharge cycles to reach their maximum discharge capacity. This can be attributed to the high lattice strain of the alloys caused by the high solidification rate because the number of H-accommodating sites decreased due to the cell distortion, which could also slow down the H-diffusion. However, the fine columnar grains of the as-spun alloys are very advantageous to the cycle life [6,7]. It is also found that the alloys with Nd or Ce had better capacity retention abilities.

Except for the abnormality in QAB_5-3, the discharge capacity of the as-spun alloys could be obviously improved by vacuum annealing because heat treatment could release the lattice stress and increase the number of the H-accommodating sites in the alloy cells. Meanwhile heat treatment could also improve the kinetic properties of the as-spun alloys because of the alleviation of the cell distortion, which can be reflected in the high-rate dischargeability test results (Fig. 6).

Except for that of QAB_5-3, the cycle life of the as-spun alloys was much improved by heat treatment because of two reasons. Firstly, the pulverization rate of the alloy powders decreased due to the alleviation of the lattice

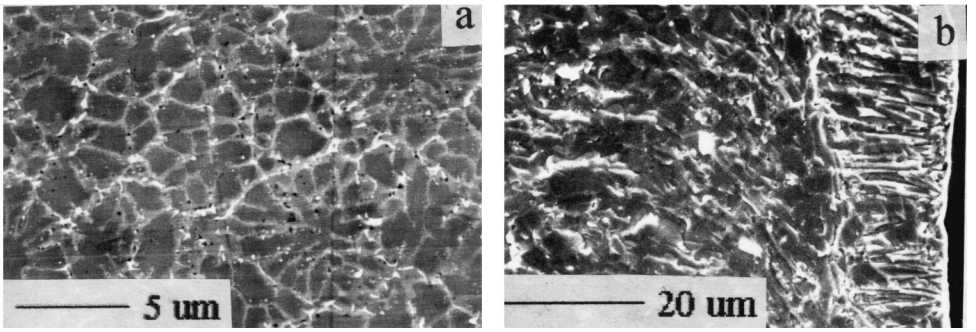

Fig. 1. The SEM images of the as-spun QAB_5-3 ribbons (a) the plane touching the cooling wheel (b) fracture.

Table 1
Element distribution in the as-spun and heat-treated alloys (at.%)

Samples	Elements	As-spun			After heat-treated at 973K		
		In grain Boundaries (at.%)	In grains (at.%)	In grain boundaries/ in grains	In grain boundaries (at.%) (at.%)	In grains (at.%)	In grain boundaries/ in grains
QAB_5-1	La	18.5	18.2	1.02	17.8	18.5	0.96
	Ni	68.7	70.8	0.97	71.6	68.0	1.05
	Co	8.73	8.49	1.03	7.34	8.26	0.89
	Sn	4.00	2.54	1.57	3.27	5.28	0.62
QAB_5-2	La	14.2	14.2	1.00	13.2	14.6	0.90
	Ni	69.3	71.7	0.97	72.1	66.7	1.08
	Co	9.61	8.37	1.15	8.25	11.2	0.74
	Nd	3.88	4.11	0.94	3.02	3.61	0.84
	Sn	3.06	1.55	1.97	3.43	3.93	0.87
QAB_5-3	La	15.2	15.0	1.01	14.7	14.9	0.99
	Ni	67.6	71.2	0.95	69.3	68.7	1.01
	Co	8.94	8.54	1.05	8.00	8.49	0.94
	Ce	3.85	3.96	0.97	3.66	3.65	1.00
	Sn	4.33	1.28	3.38	4.34	4.27	1.02

strain. Secondly, the Sn distribution was changed by heat-treatment. In alkaline solution, there is the following chemical reaction

$$Sn + 2OH^- + 2H_2O = Sn(OH)_4^{2-} + H_2\uparrow,$$

and Sn dissolved into the solution, then made the alloys deteriorate. The Sn dissolving rate could be slowed down through vacuum annealing because some of the Sn in grain boundaries diffused into grains. So the electrode acquired a stronger corrosion resistance ability and exhibited a better cycle life.

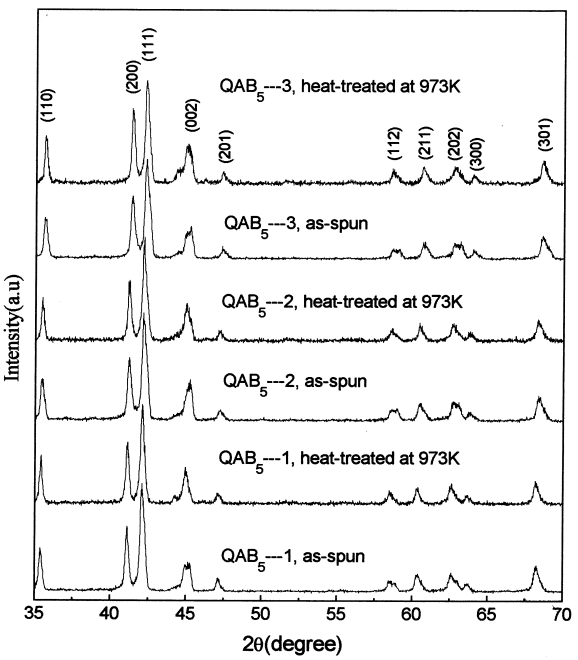

Fig. 2. XRD patterns of the as-spun and heat-treated alloys.

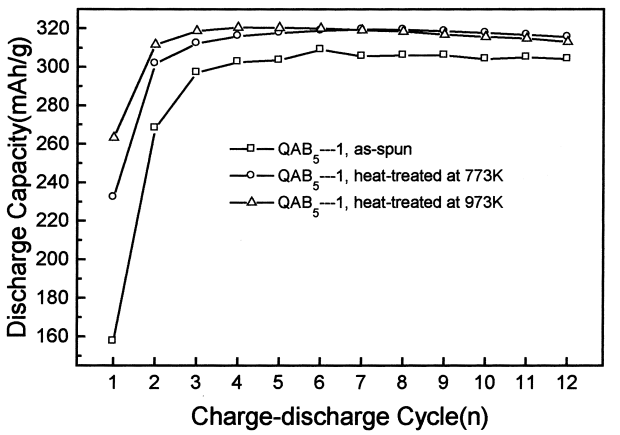

Fig. 3. Relationship between the discharge capacity and the charge–discharge cycle of the as-spun and heat-treated QAB_5-1 alloy.

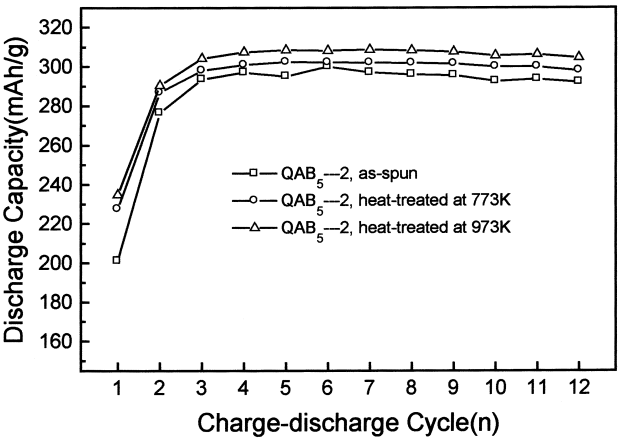

Fig. 4. Relationship between the discharge capacity and the charge–discharge cycle of the as-spun and heat-treated QAB_5-2 alloy.

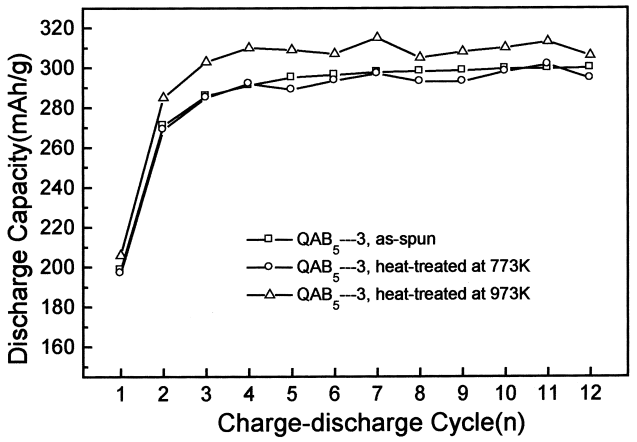

Fig. 5. Relationship between the discharge capacity and the charge–discharge cycle of the as-spun and heat-treated QAB_5-3 alloy.

Table 2
The capacity retention ability of the as-spun and heat-treated alloys after 300 charge–discharge cycles

Alloys	Alloy state	Residual capacity after 300 cycles (%)
QAB_5-1	As-spun	<60
	Heat-treated at 773K	65
	Heat-treated at 973K	63
QAB_5-2	As-spun	<60
	Heat-treated at 773K	69
	Heat-treated at 973K	70
QAB_5-3	As-spun	74
	Heat-treated at 773K	67
	Heat-treated at 973K	70

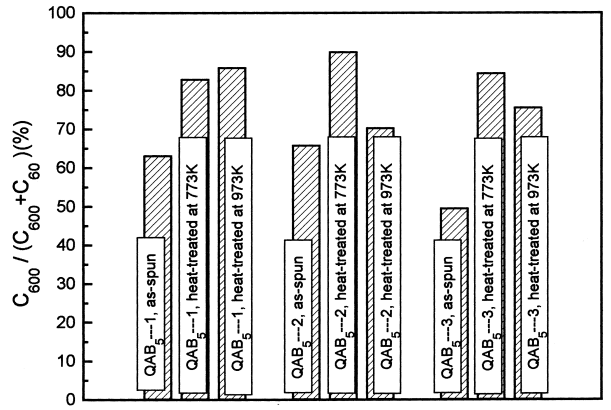

Fig. 6. High-rate dischargeability of the as-spun and heat-treated alloys.

4. Conclusion

The as-spun alloys had fine grains with Sn segregation in grain boundaries. And the Ce-containing as-spun alloy had a cycle life more than 300 cycles. The discharge capacity and kinetic properties of the as-spun alloys could be improved by vacuum annealing. And heat treatment could also improve the cycle life of the Ce-free alloy, which can be attributed to the alleviation of lattice strain and the change of the Sn distribution.

References

[1] F. Meli, A. Zuttel, L. Schlapbach, J. Alloys Comp. 190 (1992) 17.
[2] L. Jiang, F. Zhan, D. Bao, G. Qing, Y. Li, X. Wei, J. Alloys Comp. 231 (1995) 635.
[3] F. Meli, A. Zuttel, L. Schlapbach, J. Alloys Comp. 202 (1993) 81.
[4] W. Tang, Y. Gai, H. Zheng, J. Alloys Comp. 224 (1995) 292.
[5] B.V. Rathakumar, C. Witham, B. Fultz, G. Halpert, J. Electrochem. Soc. 141 (1994) L89.
[6] T. Sakai, T. Hazama, H. Miyamura, N. Kuriyama, A. Kato, H. Ishikawa, J. Less-Common Met. 172–174 (1991) 1175.
[7] T. Sakai, H. Yoshinaga, H. Miyamura, N. Kuriyama, H. Ishikawa, J. Alloys Comp. 180 (1992) 37.