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Characteristics of a cobalt-free ML(NiCuAl)$_{5.2}$ alloy obtained by different casting processing methods

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Abstract

A cobalt-free, non-stoichiometric hydrogen storage alloy of composition ML(NiCuAl)$_{5.2}$ was prepared by vacuum induction melting followed by gas atomization or the melt spinning method. The alloy powder prepared by melt spinning processing showed better cycling stability than the as-cast alloy, while the hydrogen storage capacity, electrochemical discharge capacity and activation kinetics were not significantly degraded. The alloy powder prepared by atomization processing showed a lower hydrogen storage capacity and worse comprehensive electrode performance than the melt spun alloy, probably due to the oxidation and phase segregation occurring during the atomization process. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen storage materials; Intermetallics; Rapid quenching; Powder metallurgy

1. Introduction

The development of low cobalt or cobalt-free AB$_5$-type hydrogen storage alloys as negative electrode materials in nickel–metal hydride (Ni–MH) rechargeable batteries continues to be attractive because the partial replacement of Co by other less-expensive elements or the complete elimination of Co will significantly reduce the cost of hydrogen storage alloys. However, studies [1,2] have shown that most cobalt-free alloys, particularly the Cu-containing alloys with large non-stoichiometry, generally exhibit poorer comprehensive electrode performance than the so-called 'standard alloy' [Mm(NiCoMnAl)$_5$] with 10–11 wt% cobalt, where Mm stands for Ce-rich mischmetal. Therefore, it is important to improve the performance of cobalt-free hydrogen storage alloys before the application of this kind of material in the Ni–MH battery industry becomes possible.

Some rapid solidification techniques [3–5], namely melt spinning, high-pressure gas atomization, etc. have proved to be effective in improving the compositional homogeneity and microstructure of hydrogen storage alloys. Such improvements in chemical homogeneity and microstructure, resulting from rapid solidification, enhance the electrode performance, particularly the durability in alkaline solution. In the present investigation, ML(NiCuAl)$_{5.2}$ (where ML stands for lanthanum-rich mischmetal) alloy was prepared by vacuum induction melting followed by gas atomization or melt spinning. The characteristics of the alloy powders obtained are reported.

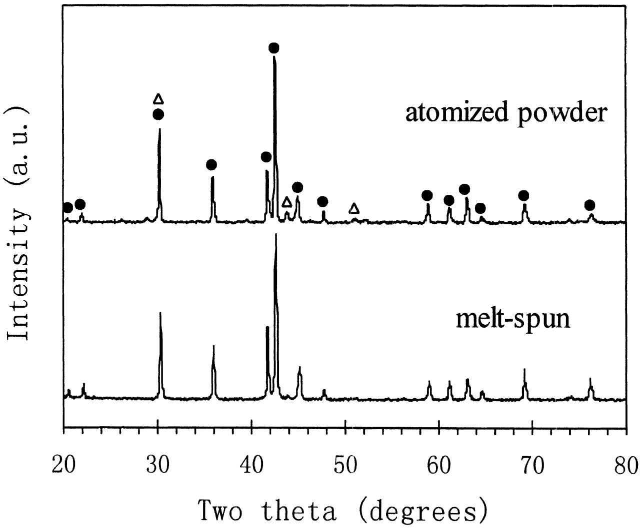

Fig. 1. X-ray diffraction patterns of the melt spun and atomized powders [(●) AB$_5$; (△) A1$_2$Cu$_3$].

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2. Experimental

The ML(NiCuAl)$_{5.2}$ alloy ingot was prepared by vacuum induction melting, using lanthanum-rich mischmetal, nickel, copper and aluminum as raw materials. One portion of the ingot was then ground into powder using a pestle and mortar and then sieved (the as-cast sample). The remaining ingots were atomized under argon of purity 99.95% into powder (the atomized sample) or melt spun into ribbons (the melt spun sample). The melt spun ribbons were then ground into powder. Finally, all powders passing a 200 mesh were used to prepare electrodes.

X-ray diffraction spectra of the various powders were obtained using an X-ray diffractometer (XRD, Philips, X'Pert MPD model) with Cu Kα radiation. Pressure–composition isotherms (*PCT* curves) of the various sam-

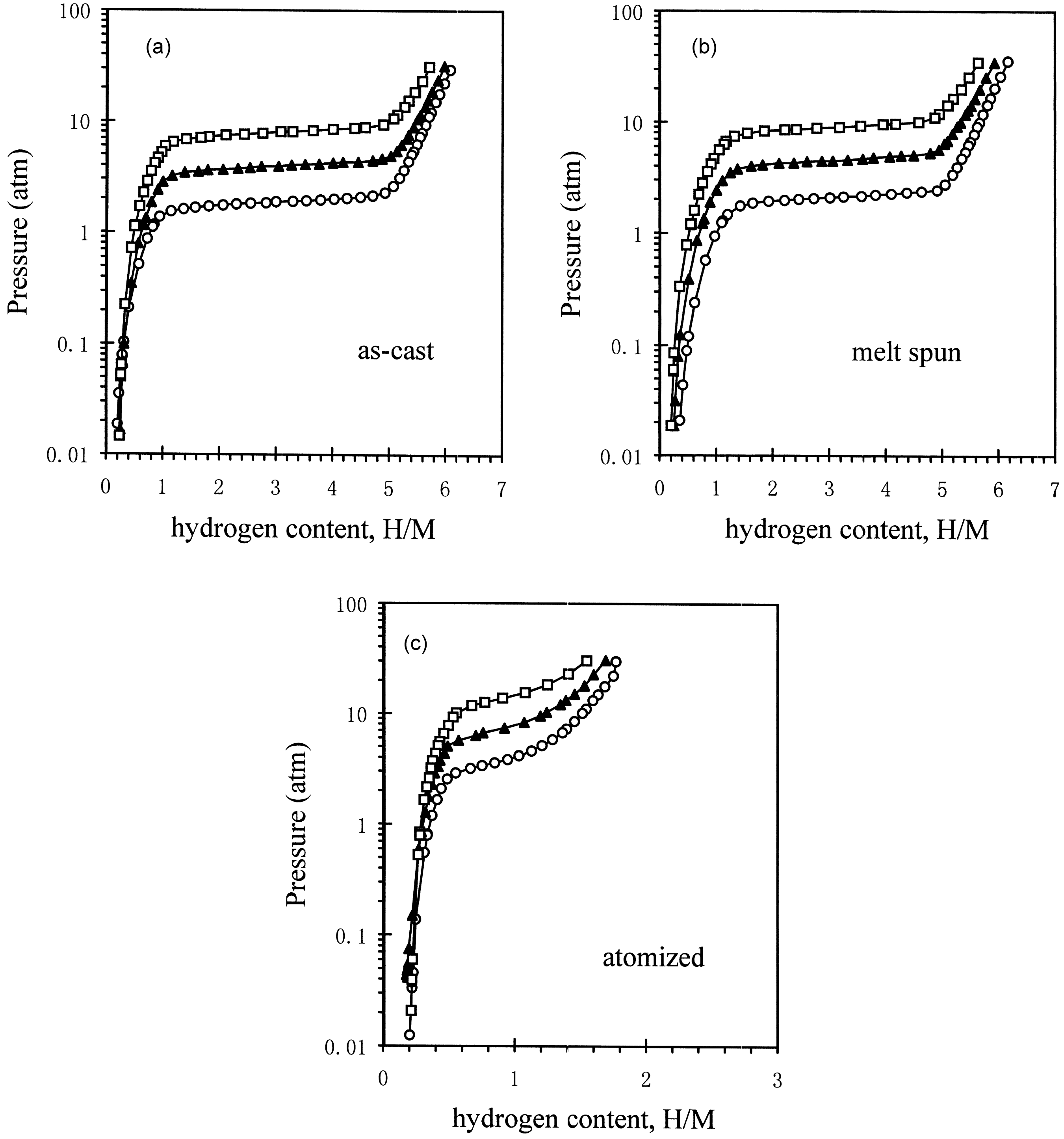

Fig. 2. Hydrogen dissociation curves for the as-cast, melt spun and atomized alloys at different equilibrium temperatures [(○) 20°C; (▲) 40°C; (□) 60°C].

ples were measured using a Sieverts-type apparatus (AMC, GRC).

The negative electrode pellets (15.5 mm in diameter) were prepared by mixing 0.3 g of alloy powder with 1.2 g of fine nickel powder, and then pressing on a piece of nickel mesh at 6 MPa for 1 min. The electrochemical measurements of these negative electrodes were performed in a half-cell with 6 M KOH solution at 20°C. A sintered nickel hydroxide electrode with capacity in excess and a Hg/HgO 6 M KOH electrode were used as counter and reference electrodes, respectively. The charge–discharge electric current was 60 mA/g and the cut-off potential for discharging was set at −0.600 V vs. Hg/HgO. The charging and discharging schedule for the cycle life measurement was as follows: charging at 300 mA/g for 1.2 h, resting 10 min and discharging at 300 mA/g until −0.600 V vs. Hg/HgO.

3. Results and discussion

The X-ray diffraction spectra of the atomized and melt spun powders are shown in Fig. 1. Both the atomized and melt spun samples are predominantly in the AB_5 phase (i.e. $CaCu_5$-type crystal structure) with a small portion in the Al_2Cu_3 phase. The amount of secondary phase is relatively higher in the atomized sample than in the melt spun sample.

The hydrogen absorption and desorption behavior for gaseous hydrogen was depicted by pressure–composition isotherms. The hydrogen dissociation curves at equilibrium temperatures of 20, 40 and 60°C for the as-cast, melt spun and atomized samples are shown in Fig. 2. It can be seen that each curve has a single pressure plateau. This indicates that all samples are mainly in a single phase, although the XRD results indicate the presence of a secondary phase in the powders. Flat plateaus are observed for both the as-cast and melt spun samples, while the atomized sample shows a sloped plateau. The origin of a sloped plateau is generally ascribed to compositional segregation [6]. The pressure plateau with a large slope, observed for the atomized sample, may be attributed to the presence of a relatively large amount of the phase in the Al_2Cu_3 structure, as indicated in Fig. 1. The presence of a relatively large amount of the secondary phase in the atomized sample is tentatively explained as follows. Insufficient purity of the argon used and the low degree of the vacuum system resulted in severe oxidation of the atomized sample. The measured oxygen content is as high as 0.25 wt%. The relatively large amount of secondary phase in the atomized sample may be caused by differential oxidation of the alloy elements because the oxidation of mischmetal is generally easier than other elements.

The plateau pressures are 0.2 (20°C), 0.39 (40°C) and 0.8 MPa (60°C), respectively, for the as-cast sample, 0.21 (20°C), 0.44 (40°C) and 0.89 MPa (60°C) for the melt spun sample, and 0.38 (20°C), 0.73 (40°C) and 1.4 MPa (60°C) for the atomized sample. The hydrogen storage capacities (20°C, 2 MPa) are 1.3, 1.4 and 0.4 wt% for the as-cast, melt spun and atomized sample, respectively.

Fig. 3 shows the activation curves of the electrodes prepared from the as-cast, atomized and melt spun powders. It can be seen that the melt spun sample shows similar activation behavior to the as-cast sample. The maximum discharge capacity is obtained after some 10 charge and discharge cycles. The atomized powder, however, shows poorer activation properties, requiring more than 40 cycles to reach its maximum capacity. The poor activation kinetics of atomized powders has also been observed by other researchers and is generally attributed to the oxidation and amorphization taking place during the atomization process [4,5,7,8]. The maximum discharge capacity of the as-cast, atomized and melt spun samples is 282, 162 and 264 mAh/g, respectively.

Fig. 4 shows the stability during charge and discharge cycling of the electrodes prepared from the as-cast, atomized and melt spun powders. The atomized and melt spun powders show better cycling stability than the as-cast sample. This is because the melt spinning and atomization processing can produce powders with a smaller grain size than those produced from conventional casting processing. After about 150 charge and discharge cycles the discharge capacity degrades 40, 29 and 17%, respectively, for the as-cast, atomized and melt spun samples. The melt spun sample, prepared at the highest cooling rate, shows the best capacity against corrosion in alkaline solution. A high cooling rate could yield a fine-grained microstructure and therefore increase the capability against corrosion in alkaline solution.

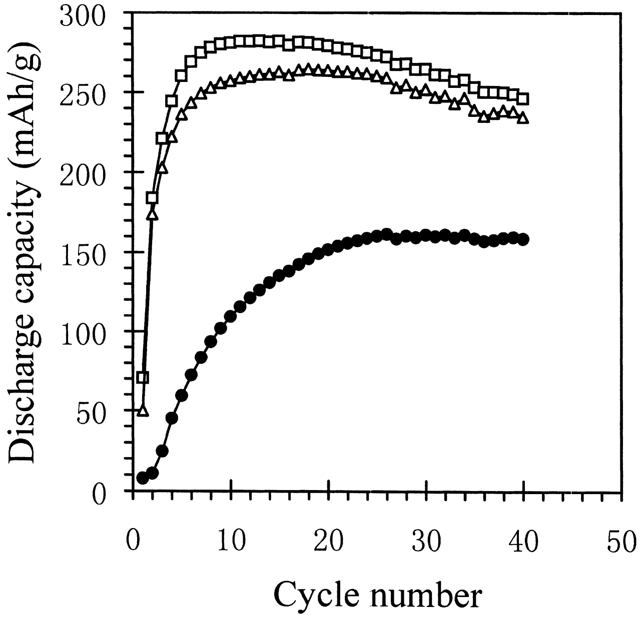

Fig. 3. Activation curves for the various alloy powders [(●) atomized; (△) melt spun; (□) as-cast].

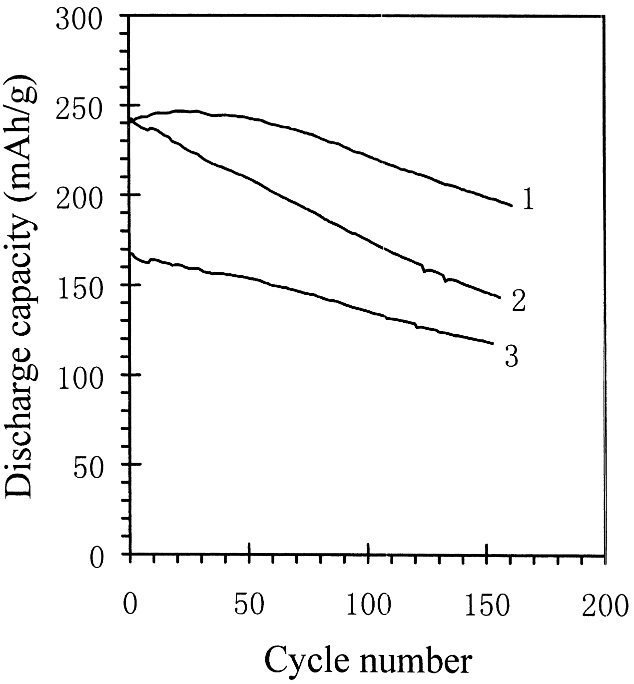

Fig. 4. Cycling stability of the electrodes prepared from various powders (1, melt spun; 2, as-cast; 3, atomized).

4. Conclusions

The cobalt-free, non-stoichiometric ML(NiCuAl)$_{5.2}$ hydrogen storage alloy powders prepared by the gas atomization and melt spinning methods showed better cycling stability over the as-cast alloy as a result of the favorable rapid solidification effects. The alloy powder prepared by the melt spinning processing showed a higher hydrogen storage capacity than that of the as-cast alloy. The electrochemical discharge capacity and activation kinetics of the melt spun alloy were comparable to those of the as-cast alloy. The alloy powder prepared by the atomization processing showed a lower hydrogen storage capacity and worse comprehensive electrode performance than the melt spun alloy, probably due to the oxidation and phase segregation occurring during the atomization process. Melt spinning processing is promising for producing a cobalt-free alloy as the potential electrode material in a nickel–metal hydride battery.

Acknowledgements

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