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Electrochemical performance of gas-atomized $MmNi_5$-based alloy powders

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Abstract

A series of $MmNi_5$-based (Mm–Ni–Co–Mn–Al) alloy powders were prepared by gas atomization. On hydrogenation, a large discontinuous volume change produced extensive fracture in all alloy powders except those smaller than 10 μm. Annealing does not affect the P–C–T characteristics, but improves the cyclic stability of the electrochemical discharge. The discharge capacity varies with the composition and particle size. There is a trade-off in the contents of Co and Mn for electrochemical performance. A higher content of Co and a lower content of Mn gives a small electrochemical capacity, but a longer cycle life. A medium content of Co and Mn results in a higher discharge capacity and decay rate. The particle size seems to be a very important factor influencing the electrochemical activation kinetics. The fracture of larger particles induced by charging creates fresh surfaces for easier hydrogenation.

Keywords: Gas atomization; $MmNi_5$-based alloy; Hydriding; Ni/MH battery

1. Introduction

In recent years, Mm-based hydrogen storage alloys have been used extensively as the negative electrode material in the Ni/MH rechargeable battery [1]. The electrochemical performance of the negative electrode is affected by the composition, stoichiometry, and microstructure of hydrogen storage alloys [2,3]. In general, cobalt in the alloy is beneficial to the cycle life [4–7], but it is the most expensive among the elements used in the Ni/MH battery. The plateau pressure can be adjusted by substituting La or Ni with other elements [8–11]. For a given composition, but prepared by different methods, the chemical homogeneity, grain size, and particle shape may play an important role in determining the electrochemical performance.

In a recently developed high-pressure gas atomization (GA) technique, the cooling rate is about 10^3–10^5 K/s [12]. The atomized powders consist of spherical particles and have different chemical and mechanical characteristics. It is believed that the gas-atomized powders show a higher chemical homogeneity and smaller grain size than those of as-cast alloys. However, it has also been reported that the atomized powders show a lower electrochemical capacity and poorer hydrogen absorption and desorption kinetics than as-cast alloys [13,14]. No large difference in the maximum discharge capacity is observed for samples with different particle sizes [15], but an increase in the decay rate of the cycle life due to pulverization of the alloy may occur. In that case, the smaller grain size can suppress the pulverization [16]. The purpose of this work was to study the gas phase and electrochemical hydriding reactions of a series of $MmNi_5$-based alloys produced by gas atomization. Activation and cyclic stability of charging/discharging were also examined.

2. Experimental

Three intermetallic compounds were studied, $MmNi_{3.6}Co_{0.84}Mn_{0.28}Al_{0.28}$, $MmNi_{3.6}Co_{0.70}Mn_{0.42}Al_{0.28}$, and $MmNi_{3.6}Co_{0.56}Mn_{0.56}Al_{0.28}$ (alloys A, B, and C, respectively). They were prepared by GA in an Ar atmosphere. For the GA process, high-pressure Ar gas was used to disintegrate a stream of molten alloy into fine powders. Some of the GA samples were further annealed at 700 or 950 °C for 1 h. A Sievert's apparatus was used to measure the pressure–composition isotherms (P–C–T curves).

The charge and discharge performance was measured in

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a test cell, which contained two pieces of positive electrode, one piece of hydrogen storage alloy as the negative electrode, and polypropylene as the separator. The electrolyte was 6 M KOH+1 wt% LiOH. The positive electrode materials consisted of nickel hydroxide, 5 wt% Co, and 5 wt% CoO. They were mixed with 3 wt% PTFE to form a paste. The negative electrode was prepared by mixing 0.5 g of active material with 3 wt% PTFE. Each paste was applied on a piece of Ni foam, and cold pressed at a pressure of 100 kgf/cm^2. Before the electrochemical experiment, the electrodes were soaked in the electrolyte for at least 1 day. The charge and discharge currents were both set at 30 mA, and the cut-off voltage was 900 mV.

3. Results and discussion

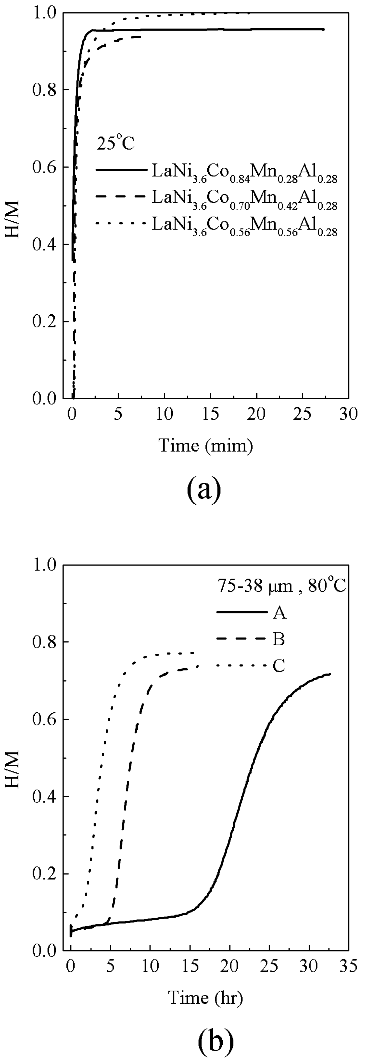
3.1. Gas-phase hydrogenation characteristics

The X-ray diffraction (XRD) patterns show that the three alloys have a pure $CaCu_5$-type structure. The peaks are all very sharp, without any second phase present in both as-prepared and heat-treated samples.

It was noted that the gas-atomized powder was very difficult to activate compared with conventional arc-melted powder, as shown in Fig. 1. For the arc-melted alloys, where La was used to substitute for Mm, it takes only a few minutes to become saturated, whereas more than 10 or even 30 h is required for the GA powders. The $P–C–T$ curves for the alloys of different particle sizes measured at 25 °C are shown in Fig. 2. The plateau pressures are significantly sloped and the hysteresis loops are all very small. The $P–C–T$ curves are essentially the same for different particle sizes, including plateau pressure, hysteresis, and width of the $\alpha–\beta$ region, but the hydrogenation capacities for smaller particles are slightly lower than those of larger ones. The equilibrium pressure of alloy A is the highest. The plateau pressure decreases with increasing Mn content. Although substitution of Ni by Co may reduce the plateau pressure, its effect is not significant [17]. The lowest plateau pressure of alloy C can be attributed mainly to greater substitution of Mn for Ni.

The SEM morphologies of the gas-atomized alloy powders for alloy C before and after the $P–C–T$ test are shown in Fig. 3. The other two alloy powders show the same feature. It can be seen that the as-prepared atomized particles are spherical. After the $P–C–T$ measurement, the larger particles were pulverized into many irregular pieces. For particles just larger than 10 μm, cracks are formed but the integrity is maintained. For particles smaller than 10 μm, they remain the same shape and crack free. Therefore, 10 μm is probably the critical size for exhibiting different hydrogenation properties.

The alloy powders, without sieving, were then subjected to heat treatment at 700 °C for 1 h. The $P–C–T$ curves basically did not change much compared with those of as-prepared alloys. Alloys B and C appear to have larger capacities than alloy A after annealing.



(a)

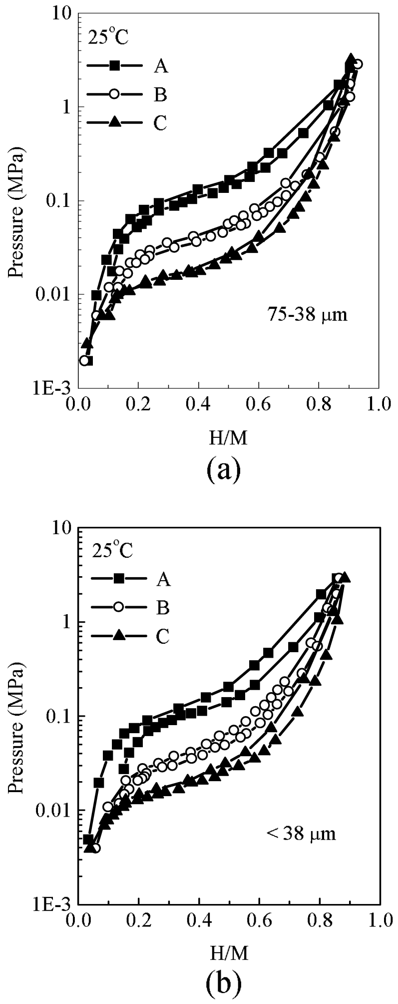
(b)

Fig. 1. Hydrogenation kinetic curves of various alloy powders. (a) Arc melted, (b) gas atomized.

3.2. Electrochemical performance

The electrochemical discharge capacities of the three compositions without sieving were measured first. After 60 cycles of test, alloy B had the highest capacity (~250 mAh/g), followed by alloys C (~230 mAh/g) and A (~100 mAh/g). In general, Co improves the cycle life but reduces the capacity, and Mn increases the capacity but is detrimental for the cyclic life because it may dissolve in the KOH solution. In order to design an optimum composition for the electrode, there is a trade-off in the contents of Co and Mn for better performance.

Since alloy A had a much lower discharge capacity, which may be due to its high plateau pressure, alloys B and C were selected to study the particle size effect. For the same composition, the activation performance of



(a)

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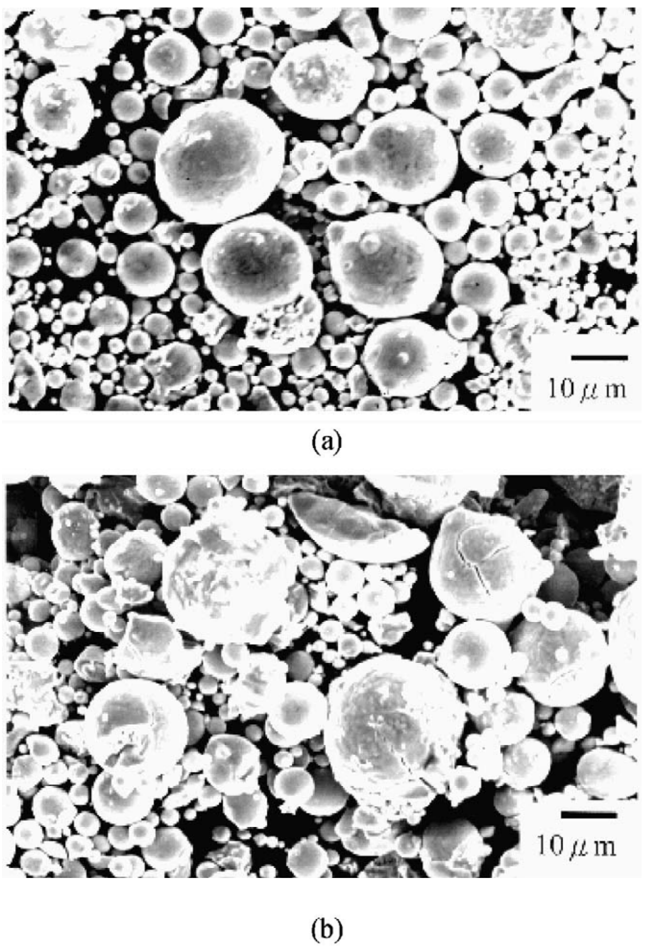
Fig. 2. $P-C-T$ curves of gas-atomized powders with different particle sizes. (a) 75–38 μm, (b) <38 μm.



(a)

(b)

Fig. 3. SEM micrographs of alloy C with particle size <38 μm. (a) As-prepared, (b) after the $P-C-T$ test.

smaller particles is poorer, as shown in Fig. 4. It takes only 20 cycles to achieve the maximum capacity for larger particles (75–38 μm) of both alloys B and C. On the other hand, it takes more than 80 cycles to obtain the maximum capacity for smaller particles (<38 μm). The cyclic stability of smaller particles, however, is better than that of larger particles. This could be due to the greater pulverization of the larger particles.

Fig. 4 also shows the discharge capacities of alloys B and C that were annealed at 950 °C for 1 h (designated B′ and C′, respectively). The cyclic stability is improved by the annealing for all samples. This is especially pronounced for alloy C, the decay rate of which is quite high for larger particles. Annealing essentially eliminates the decay in the discharge capacity. Generally speaking, the higher capacity of alloy C is caused by the greater content of Mn.

The surface morphologies of two electrodes made of alloy C after the electrochemical test are shown in Fig. 5. The larger particles (75–38 μm) were fragmented into many smaller pieces, although each original particle geometry was maintained. For smaller particles less than 10 μm, no cracking occurs. Only a few creaks are observed for particles between 38 and 10 μm. This may be the reason why the activation rate for larger particles is faster than that of smaller particles. The fresh surface created in the larger particles during charge–discharge makes the reaction with hydrogen and OH^- proceed more readily.

It was also observed that the original surface of larger particles was rougher. They are easier to activate than the smaller particles. There have been a number of reports dealing with the surface effect on the electrochemical hydrogenation properties of GA powder. For instance, Li et al. pointed out that rapid quenching usually makes activation more difficult, but the cyclic stability can be increased [16]. Mishima et al. reported that, for quenched alloys, the grain boundaries provide a fast diffusion path for hydrogen to activate the electrode at a higher rate and result in a higher discharge capacity [18]. On the other hand, Huang and Zhang [15] reported that gas-atomized powders with a small particle size (14.1 μm) have good activation performance, but the maximum discharge capacity is only 130 mAh/g. Although the results are

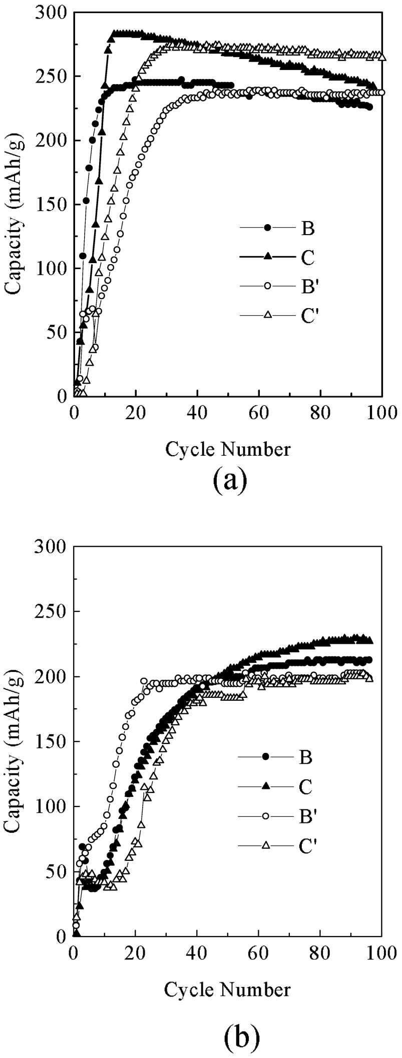


Fig. 4. Discharge capacities of as-prepared (B and C) and annealed (B′ and C′) alloy powders. (a) 75–38 μm, (b) <38 m.

somewhat contradictory, they all illustrate that the surface condition for the GA powders is very important for hydrogenation. The present result as a function of particle size seems to indicate that the kinetic performance of GA powders depends on their surface state.

4. Conclusions

1. The gas-atomized alloys A, B, and C are more difficult to activate in gas hydrogenation than arc-melted alloys. The *P–C–T* curves are different because of the different contents of Co and Mn. There is not much difference in the *P–C–T* curves for alloys with different particle sizes. Annealing does not affect the *P–C–T* characteristics very much.
2. In the electrochemical test, the particle size seems to be an important factor influencing the electrochemical activation kinetics. There is a trade-off in the contents of Co and Mn for the electrochemical performance. A higher content of Mn shows a higher capacity, but also a higher decay rate. Increasing the content of Co can improve the cyclic stability. Annealing improves the cyclic stability, but the maximum capacity is slightly reduced.

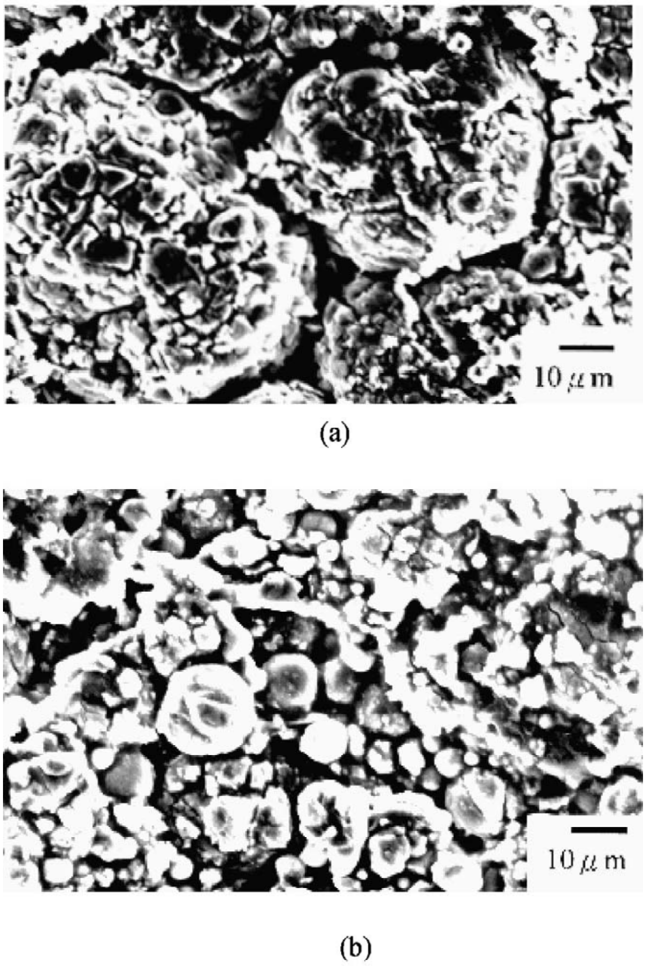


Fig. 5. SEM morphologies of alloy C after the electrochemical test. (a) 75–38 μm, (b) <38 μm.

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References

[1] T. Sakai, H. Yoshinaga, H. Miyamura, H. Ishikawa, J. Alloys Comp. 180 (1992) 37.
[2] P.H.L. Notten, P. Hokkeling, J. Electrochem. Soc. 138 (1991) 1877.
[3] Y. Fukumoto, M. Miyamoto, M. Matsuoka, C. Iwakura, Electrochim. Acta 40 (1995) 845.

[4] J.J.G. Willems, Philips J. Res. 39 (1984) 37.

[5] M. Kanda, M. Yamamoto, K. Kanno, Y. Satch, H. Hayashida, M. Suzuki, J. Less-Common Met. 172–174 (1991) 1227.

[6] M. Latroche, A. Percheron-Guégan, Y. Chabre, J. Alloys Comp. 293–295 (1999) 637.

[7] H. Pan, J. Ma, C. Wang, S. Chen, X. Wang, C. Chen, Q. Wang, J. Alloys Comp. 293–295 (1997) 648.

[8] F. Meli, A. Zuettel, L. Schlapbach, J. Alloys Comp. 190 (1992) 17.

[9] M.P. Sridhar Kumar, H. Oesterreicher, L.Y. Zhang, J. Alloys Comp. 216 (1994) 21.

[10] G.D. Adzic, J.R. Johnson, J.J. Reilly, J. McBreen, S. Mukerjee, M.P. Sridhar Kumar, W. Zhang, S. Srinivasan, J. Electrochem. Soc. 142 (1995) 3429.

[11] J. Wu, J. Li, W. Zhang, F. Muo, L. Tai, R. Xu, J. Alloys Comp. 248 (1997) 180.

[12] I.E. Anderson, M.G. Osborne, T.W. Ellis, JOM (1996) 38.

[13] R.C. Bowman Jr., C. Witham, B. Fultz, B.V. Ratankumar, T.W. Ellis, I.E. Anderson, J. Alloys Comp. 253/254 (1997) 613.

[14] Y.M. Solonin, V.V. Savin, S.M. Solonin, V.V. Skorokhod, L.L. Kolomiets, T.I. Bratanich, J. Alloys Comp. 253/254 (1997) 594.

[15] Y. Huang, H. Zhang, J. Alloys Comp. 305 (2000) 76.

[16] C. Li, X. Wang, X. Li, C. Wang, Electrochim. Acta 43 (1998) 1839.

[17] T. Sakia, K. Oguro, H. Miyamura, N. Kuriyama, A. Kato, H. Ishikawa, C. Iwahura, J. Less-Common Met. 161 (1990) 193–202.

[18] R. Mishima, H. Miyamura, T. Sakai, N. Kuriyama, H. Ishikawa, I. Uehara, J. Alloys Comp. 192 (1993) 176.