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Highly densed-MH electrode using flaky nickel powder and gas-atomized hydrogen storage alloy powder

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Abstract

Hydrogen storage alloy powder is used as the negative electrodes of nickel–metal hydride (Ni–MH) secondary batteries. This powder consists of irregularly-shaped, angular particles. Hence when packing it into an electrode, gaps are formed between the particles, and the powder is not compacted to high density. In order to pack the alloy powder to high density, an alloy powder with spherically-shaped (AB_5-type alloy) particles has been developed. The spherical particles are fabricated using a gas atomizer device. Further, a metal powder with flake-shaped particles has developed as a conducting material to enable efficient electrode conduction. The latter powder adheres to the spherically-shaped alloy particle surfaces to form a conducting network within the electrode. By combining 95% spherical-type hydrogen storage alloy powder with 5% flake-type nickel powder, then intermixing a polytetrafluoroethylene (PTFE) resin binder at 1 wt.% and compression-molding, an electrode was obtained with a discharge capacity of 1808 A h l^{-1}.

Keywords: Flake nickel powder; Flake copper powder; Hydrogen storage alloy powder; Gas-atomized powder; Nickel–metal hydride electrode

1. Introduction

The authors have developed flake-type copper and nickel powders as conductive materials for Ni–MH secondary batteries [1–3]. When using these powder materials to fabricate electrodes, a three-dimensional conductive network structure is formed by using the flake-type powder in the electrode, so that conductivity is improved. As a result, discharge capacities 10% higher than electrodes using conventional nickel powder are obtained.

In this research, a hydrogen storage alloy powder with spherically-shaped particles was developed in order to further improve the discharge capacity per unit volume. In addition, a nickel powder with flake-shaped particles was heat-treated and softened to obtain a new powder material, in which powder is compacted to form negative electrodes. Here the spherical powder particles are in point contact, so that a thin green compact cannot be formed. Hence a PTFE resin was used as a binder.

These materials were employed with electrode fabrication techniques to fabricate negative electrodes, and the effect of the powder particles shape was studied based on the electrode discharge capacity.

2. Experimental details

The spherical-type hydrogen storage alloy powder was fabricated using a gas atomize device. Argon was used as the gas. The mean particle diameter of the atomized powder particles was 57 μm. Table 1 shows the chemical analysis results. This powder was crushed to irregularly-shaped particles in an argon gas atmosphere. Lightly-crushed (low ground) powder was also prepared. The characteristics of each of these powders are shown in Table 2 and Fig. 1. Flake-type copper powder and nickel powder were prepared using a mechanofusion machine

Table 1
Chemical analysis of hydrogen absorbing alloy made by gas atomization method

Chemical analysis (mass%)										
La	Ce	Pr	Nd	Ni	Co	Mn	Al	O	C	Other
19.0	4.4	3.5	6.6	49.3	9.9	4.9	2.1	0.02	0.01	0.27

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Table 2
Properties for hydrogen absorbing alloy powders produced by gas atomization

Properties	As atomized	Low ground	Ground
Particle size (μm)	57.9	50.9	37.9
Apparent density (g cm^{-3})	4.10	4.00	3.11
Tap density (g cm^{-3})	5.00	4.95	4.54
Green density[a] (g cm^{-3})	6.53	6.50	6.15

[a] Test piece: 16 ϕ, 1 g; compacting pressure, 490 MPa; binder/lubricant, 1.0 mass%, PTFE.

Table 3
Properties of nickel and copper powders

Properties	Flake Ni	Filamentary Ni	Dendritic Cu
Particle size (μm)	11.0	12.6	2.3[a]
Sphsiency[b] (cm^2 g−1)	21 300	18 400	5100
Apparent density (g cm^{-3})	0.9	0.8	0.9
Tap density (g cm^{-3})	2.47	0.41	1.69
Green density[c] (g cm^{-3})	7.13	5.46	–

[a] Fisher save sieve sizer.
[b] BET sphsiensitic surface area.
[c] Test piece: 16 ϕ, 1 g. Compacting pressure: 490 MPa.

(Hosokawa Micron Co. Ltd., Model AM-15F) in an argon gas atmosphere for 2.0 h. For comparison, conventional filament-type nickel powder was also used. The characteristics of each of these powders are shown in Table 3 and Fig. 2. The alloy powder (1 g), flake-type powder (3 g) and PTFE resin binder were then intermixed and compacted to form MH electrodes (Fig. 3).

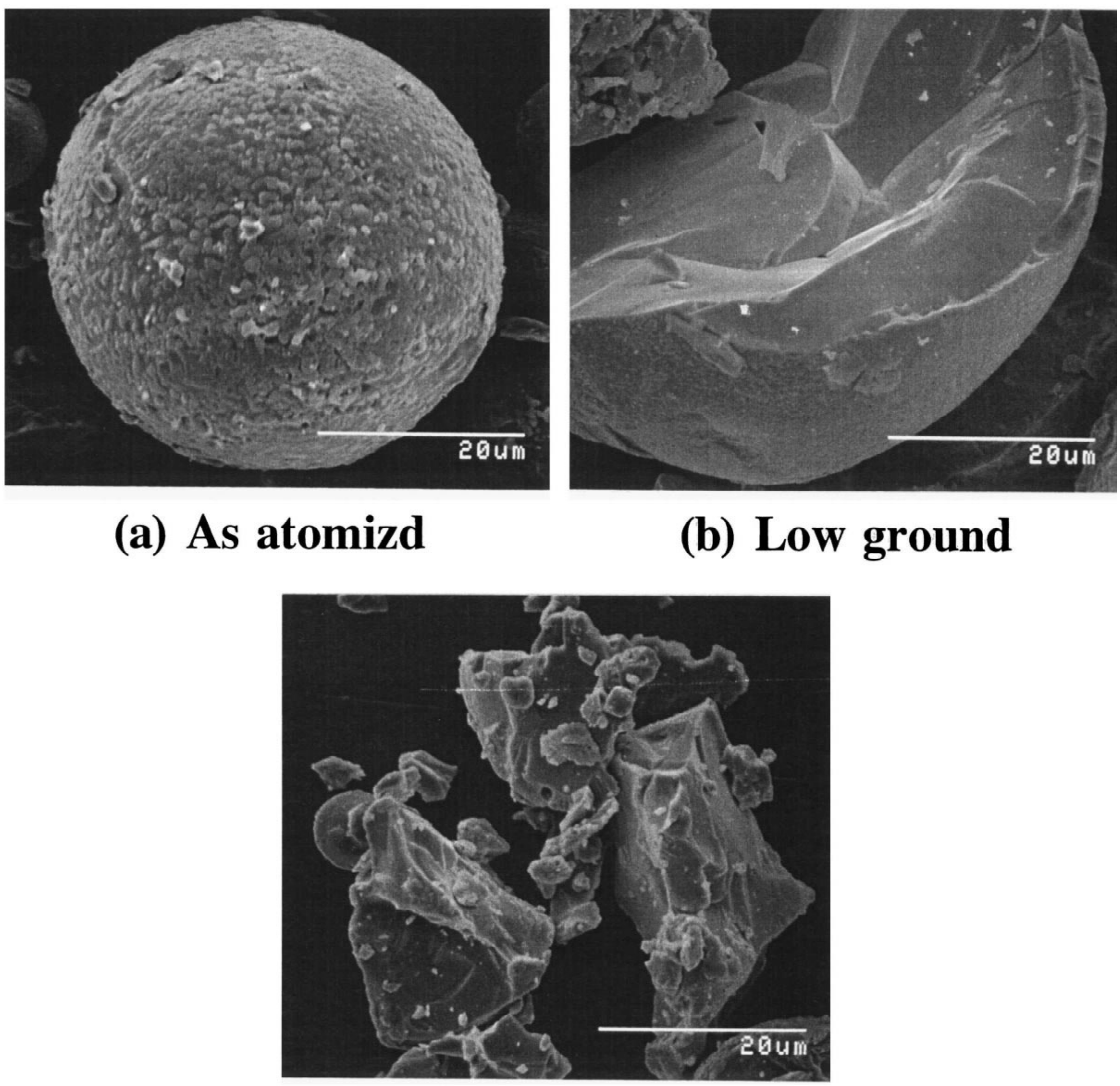
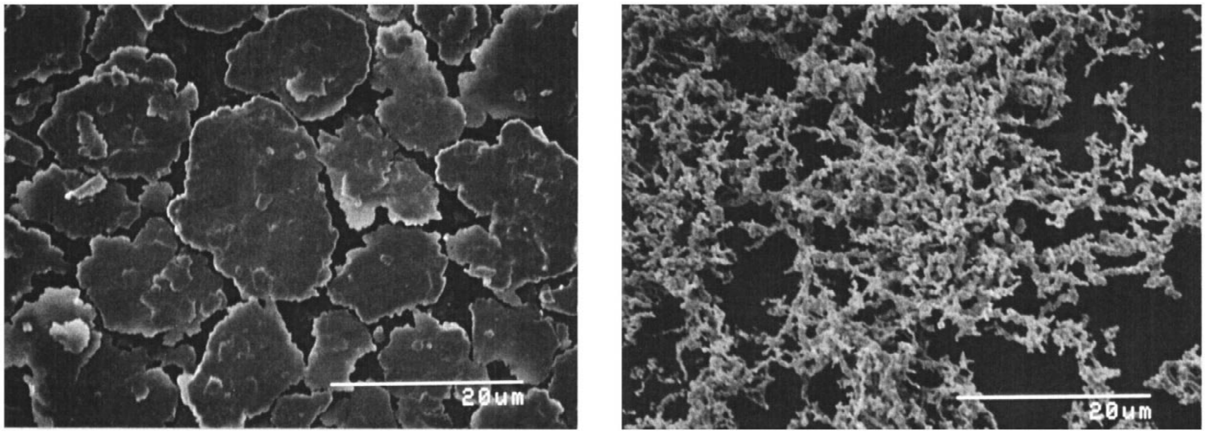


Fig. 1. SEM photographs of hydrogen absorbing alloy powders made using various grinding conditions.



(a) Flake nickel powder (b) Filamentary nickel powder

Fig. 2. SEM photographs of conductive flake nickel powder and filamentary nickel powder.

The electrochemical properties were tested in a MH-limited open cell using 6 M KOH in which the MH electrode was sandwiched between two nickel electrodes. The cell was charged at 100 A kg^{-1} for 4 h, rested for 0.5 h, and then discharged at 100 A kg^{-1} down to 0.8 V. Metallographic examinations were performed by using a scanning electron microscope and optical micrographs.

3. Results and discussion

Atomized powder, and powder obtained by crushing this in argon gas, were prepared, and the effects of the particle surface (rupture surface) on the charge/discharge cycle characteristics was investigated. MH-electrode were prepared by mixing 1 g of each alloy with 3 g of dendritic copper powder and compacting, and these electrodes were tested; the results appear in Fig. 4.

In the electrode (A) using the atomized powder, the particle surfaces were oxidized, initial activation was slow, and the number of cycles to reach the maximum discharge capacity was the greatest. The electrode (B), fabricated by crushing the atomized powder in argon gas, producing new ruptured surfaces in some of the particles, and using this powder in electrode, had faster initial activation than electrode (A), and required only a relatively small 15 cycles to reach maximum discharge capacity. The discharge capacity up to 200 cycles was nearly the same as that of the electrode (A). On the other hand, the electrode (C), fabricated from powder obtained by producing fresh ruptured surfaces on many of the particles obtained by crushing the atomized powder in argon gas to 63 μm or

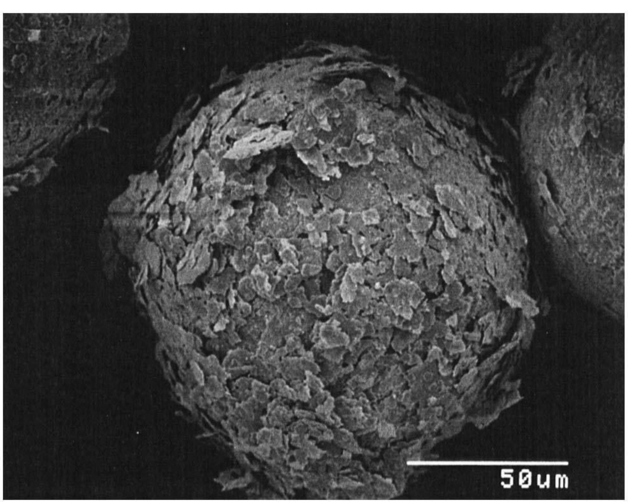


Fig. 3. SEM photographs of flake nickel, spherical alloy and PTFE resin made by milling.

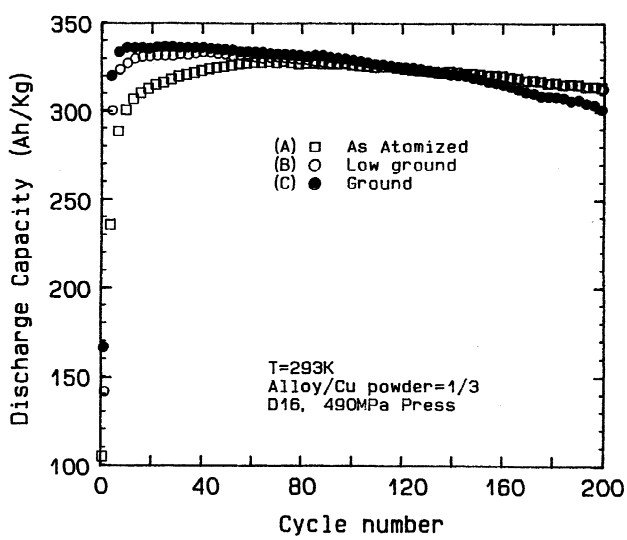


Fig. 4. Discharge capacity vs. cycle number curves for metal hydride electrodes made using hydrogen absorbing alloy ground in various conditions.

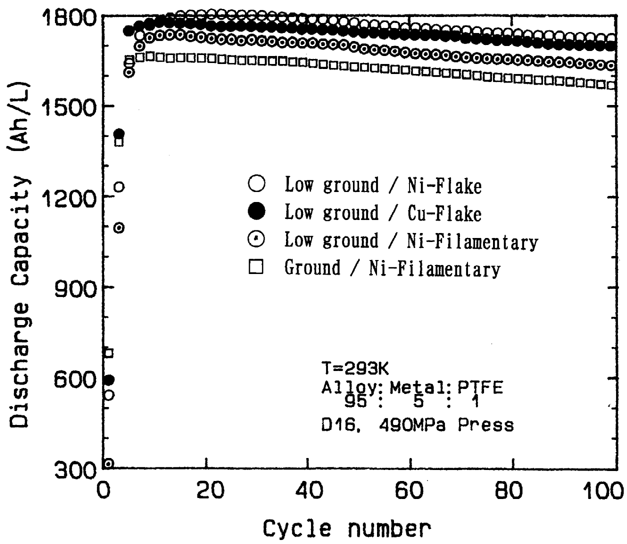


Fig. 5. Discharge capacity vs. cycle number curves for metal hydride electrodes made with various additives.

less, exhibited the fastest initial activation, and only 12 cycles were required to reach maximum discharge capacity. However, after about 160 cycles the discharge capacity began to drop far below that of the other electrodes. The results of lifetime tests of electrode (B) appear in Fig. 2. Even after 1000 cycles, the discharge capacity remained at 166 A h kg^{-1}, half the maximum value.

The differences in packing amounts due to different alloy particle shapes were investigated through measurements of different densities. The results are shown in Table 2 and Fig. 1. The atomized powder has a high apparent density since the particles are spherical in shape (Fig. 1 (a: as atomized)), so that a large amount can be packed together. In the lightly crushed or low ground powder (Fig. 1 (b: low ground)), some of the spheres are ruptured to hemispherical or angular shapes with a lower apparent density than the powder atomized (Fig. 1(a)). The powder (Fig. 1 (c: ground)), crushed completely to irregular shapes (Fig. 1 (c: ground)), had the lowest apparent density, since gaps were formed between powder particles on packing.

The effect of the shape of the conductive metal particles on the discharge capacity per unit volume has been studied. The discharge capacity of MH-electrodes formed using flake-type metal powder and filamentary powder is shown in Figs. 5 and 6. The flake-shaped particles make face contact with the alloy particles to form a conductive network. Because the alloy particles are covered by the thin flake-shape particles, gaps between particles are narrow, and packing density is high (Fig. 6(a)). On the other hand, filament-type powder makes point contact, and gaps between particles are large, so that packing densities are low and the discharge capacity per unit volume is also low (Fig. 6(b)).

4. Conclusions

Powder formed by lightly crushing hydrogen storage

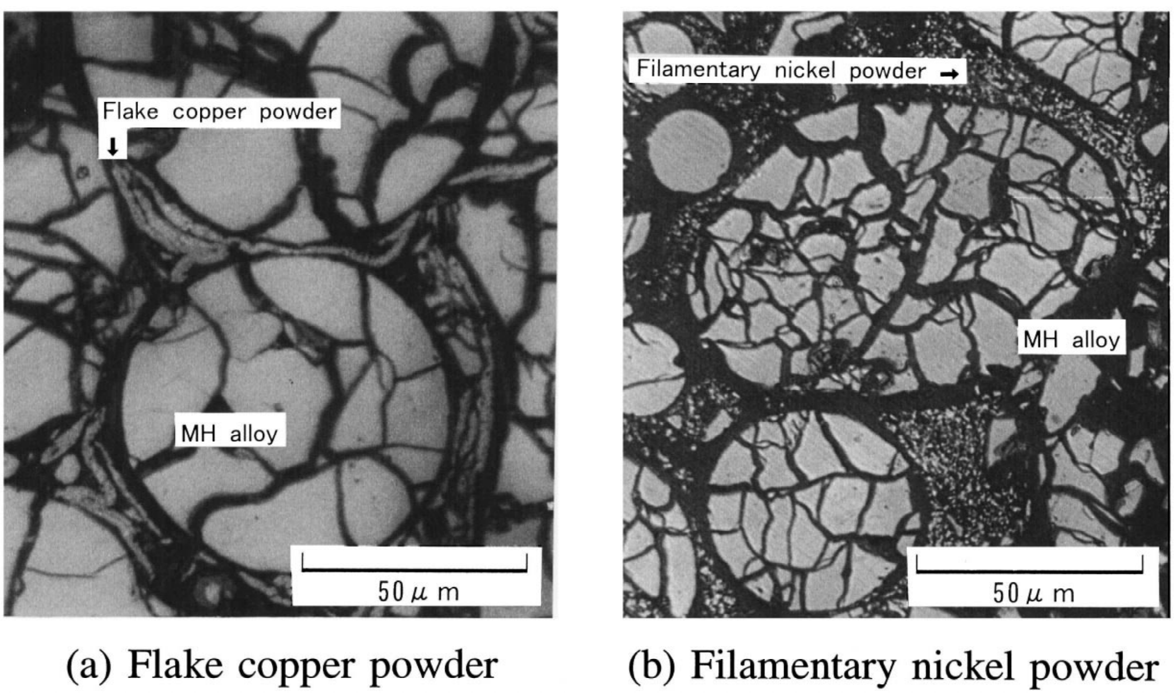


Fig. 6. Optical micrographs of cross-section of metal hydride electrodes made with copper flake powder and filamentary nickel powder (after 500 cycles).

alloy powder with spherical particles has a high packing density and a high discharge capacity per unit volume.

Flake-shaped metal particles make face contact surrounding spherical alloy particles, reducing the contact resistance and improving electrical conductivity. A conductive network is formed and improves electrical collection performance.

Use of compaction molding to fabricate MH-electrodes makes possible compact electrodes at reduced costs.

References

[1] H. Yoshinaga, M. Wada, T. Sakai, H. Miyamyra, N. Kuriyama, I. Uehara, Denki kagaku 63 (1995) 847.

[2] H. Yoshinaga, M. Wada, T. Sakai, H. Miyamyra, N. Kuriyama, I. Uehara, J. Alloys Comp. 253–254 (1997) 665–667.

[3] H. Yoshinaga, M. Wada, T. Sakai, I. Uehara, Electrode for Alkali Secondary Battery and Method for Producing the Same, U.S. Patent 5905004.