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Short Communication

Effect of annealing on the hydrogen-storage properties of rapidly quenched AB_5-type alloys

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Abstract

The effect of annealing on the hydrogen-storage properties of rapidly quenched AB_5-type alloys is investigated by electrochemical measurements and X-ray diffraction. Annealing affects discharge capacity, voltage and cycle life. Annealing at an appropriate temperature can give a promising alloy with large capacity, high discharge voltage and long cycle life. Annealing at too high a temperature, such as 800 °C, results in the largest discharge capacity but the worst cycle life. Annealing can also flatten the discharge plateau regions. The striking difference in the phase structure between as-quenched and as-annealed alloys is that new phases occur as the product of annealing at high temperatures such as 600 and 800 °C. These phases are responsible for the deterioration in cycle durability. © 1998 Elsevier Science S.A.

Keywords: Metal hydrides; Alloys; Quench; Anneal; Negative electrodes

1. Introduction

Nickel/metal-hydride systems using hydrogen-storage alloys have received considerable attention as high capacity batteries [1]. Mm-based (Mm = Mischmetal) AB_5-type hydrogen-storage alloys are practical negative electrode materials and are widely applied. The performance depends on the cast conditions as well as on the alloy composition, but differing results have been reported [2–7]. In the authors' former work [3] was found that rapid quenching by a melt-spinning method leads to a small decrease in capacity and lower discharge potentials than those of the master alloy, though it produces a much longer cycle life. The aim of this work is to find the means to overcome both the capacity and the discharge potential limitations.

2. Experimental

A base ingot of the $MmNi_{3.8}Mn_{0.55}Co_{0.6}Ti_{0.05}$ alloy was prepared by induction melting and cooled in a copper mould which was cooled by water. All the raw materials had a purity of > 99.9%. Ribbons of the alloy (thickness 40-60 μm) were produced by the use of a melt-spinning machine with a copper roller under an argon atmosphere. The rapidly quenched alloy was annealed in a vacuum for 1 h at 400, 600 and 800 °C, respectively. The alloy samples were ground into powders with a diameter of about 70 μm for electrochemical measurements and 50 μm for X-ray powder diffraction (XRD) measurements.

Electrode pellets (11 mm in diameter) were prepared by mixing 1 g of alloy powder with fine nickel powder in a weight ratio of 1:1, together with a small amount of polyvinyl alcohol (PVA) solution as a binder, and then pressing at 3500 kgf cm^{-1} after vacuum drying at 80 °C for 1 h. Before the electrochemical measurements, the sample electrodes were immersed in the electrolyte for at least one day in order to wet fully the electrode. To prevent the electrode plate breaking into pieces during charge/discharge cycling, it was clamped and pressed by porous nickel. A sintered nickel hydroxide ($Ni(OH)_2$/NiOOH) plate served as the counter electrode and a Hg/HgO 6 M KOH electrode as the reference electrode. All potentials are reported with respect to the latter electrode. Multiple constant charge/discharge currents were applied for the measurements of the discharge capacity and cycle life, together with the discharge potential [3]. The end of discharge was set at −0.500 V. Every

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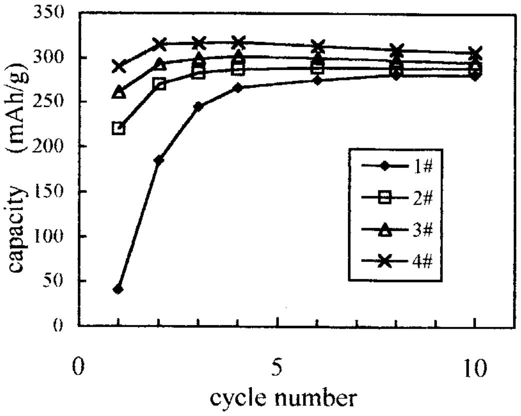

Fig. 1. Discharge capacity during the first ten cycles with a constant charge/discharge current of 60 mA g^{-1}: (#1) alloy in as-quenched state; alloys annealed for 1 h at (#2) 400 °C, (#3) 600 °C, and (#4) 800 °C.

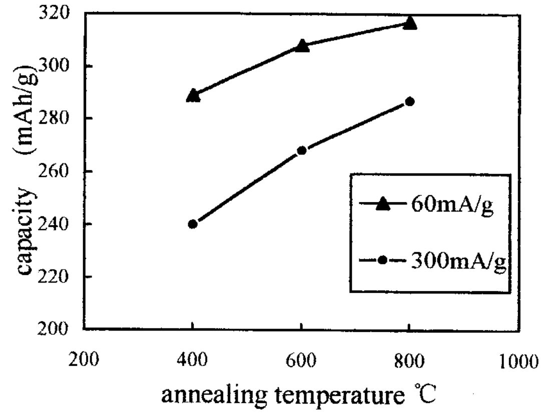

Fig. 3. Maximum discharge capacity as a function of annealing temperature with discharge rates of 60 and 300 mA g^{-1}.

cycle was performed by charging fully and discharging to −0.500 V, at a fixed temperature of 25 °C.

The crystal structure of the alloy powders before charge/discharge cycling was identified by XRD experiments with Co Kα_1 radiation.

3. Results and discussion

The activation rate of the alloys in as-quenched state and in as-annealed state with different annealing temperatures is shown in Fig. 1. The data show that annealing makes the alloy activate more easily and: the higher the annealing temperature, the easier the activation. A higher discharge voltage and a larger maximum discharge capacity can also be obtained by annealing (Figs. 2 and 3). Furthermore, annealing can flatten the discharge plateau region: the higher the annealing temperature, the flatter the plateau (Fig. 2).

The discharge-rate dependence of the capacity is given in Fig. 4. Annealing raised the discharge capacity, especially at high discharge rates. It should be noticed that, compared with the as-quenched alloy, the alloy annealed at 400 °C has roughly the same capacity at a discharge rate of 60 mA g^{-1}, but has a much larger capacity at 300 mA g^{-1}. In fact, the capacities at a high discharge rate, such as 300 mA g^{-1}, for all annealed alloys are generally raised by larger amounts than those at a low discharge rate of 60 mA g^{-1} after annealing. This suggests that annealing enhances the high-rate discharge capability.

Annealing also causes larger changes in cycle life (Fig. 5). The alloy annealed at 400 °C for 1 h shows the best charge/discharge durability in all samples and its capacity and discharge voltage are also promising. The alloys annealed at higher temperatures display very poor cycle durability, especially the alloy annealed at 800 °C which has the largest capacity at both low (60 mA g^{-1}) and high (300 mA g^{-1}) discharge rates (Figs. 3 and 4). The stability of the alloy annealed at 600 °C decreases to the level of the cast alloy [3]. Thus, there is an optimum annealing temperature to gain the best performance from the quenched alloy.

A study of the structure and microstructure was undertaken in order to explain the above phenomena. The XRD

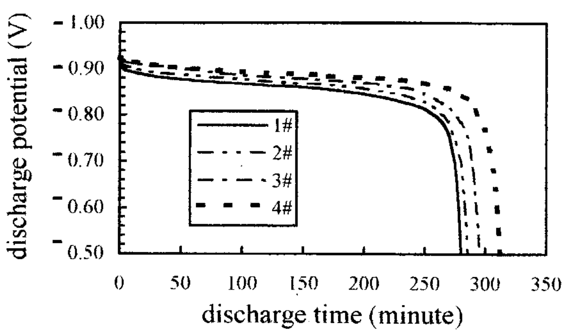

Fig. 2. Discharge characteristics of electrodes made from alloys both in as-quenched state (#1) and in as-annealed state ((#2) 400 °C; (#3) 600 °C; (#4) 800 °C) with a constant discharge current of 60 mA g^{-1} at 25 °C after all electrodes have been activated completely.

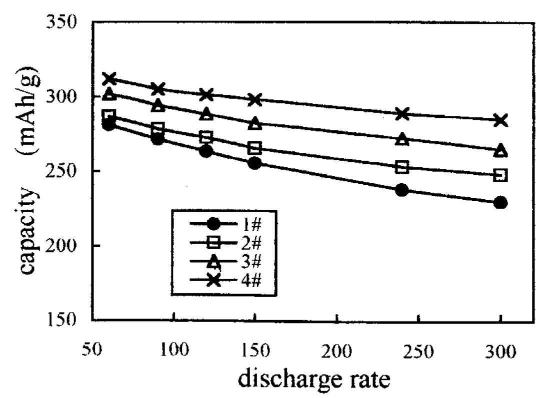

Fig. 4. Discharge rate dependence of capacity at 25 °C of alloys in as-quenched (#1) or as-annealed state ((#2) 400 °C; (#3) 600 °C, and (#4) 800 °C).

spectra of the alloys in both the as-quenched and the as-annealed states are presented in Fig. 6. Obviously, the dominant phase of all alloys can be easily indexed to the AB_5-type with $CaCu_5$ structures. Nevertheless, striking differences can be observed in the diffraction patterns. First, the alloy annealed at 400 °C has almost the same pattern as that of the as-quenched alloy, but high annealing temperatures, such as 600 and 800 °C, exhibit differences in that peaks at 2θ angles of 51.6° and 89.5° are present, especially in the alloy annealed at 800 °C for which these peaks have relatively high intensities. Moreover, the latter has a peak at a 2θ angle of 54.4°, as is found in the master alloy [3]. These peaks suggest that new phases are produced by annealing. The new phases should account for the sharp decrease in cycle durability because no other changes in phase structure are caused by annealing. This is therefore concluded that annealing can improve the hydrogen-storage property when it does not lead to a phase transition. Second, annealing can narrow the width of the peaks and promote changes in intensity. The width of the peaks of alloy annealed at 800 °C is the narrowest and, thereby, the intensity becomes very strong. This can be

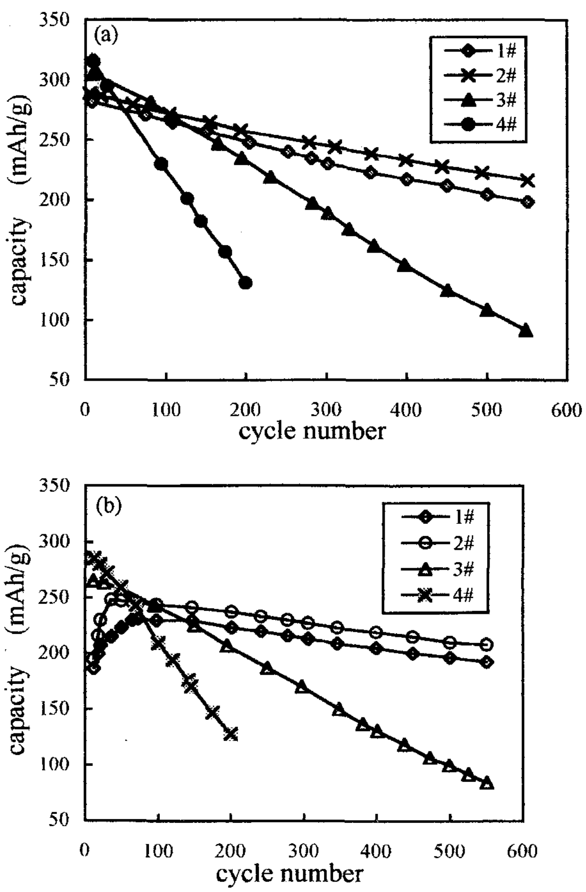

Fig. 5. Capacity vs. cycle number for as-quenched (#1) and as-annealed ((#2) 400 °C; (#3) 600 °C, and (#4) 800 °C) alloy electrodes at 25 °C. Discharge rate: (a) 60 mA g^{-1}, and (b) 300 mA g^{-1}.

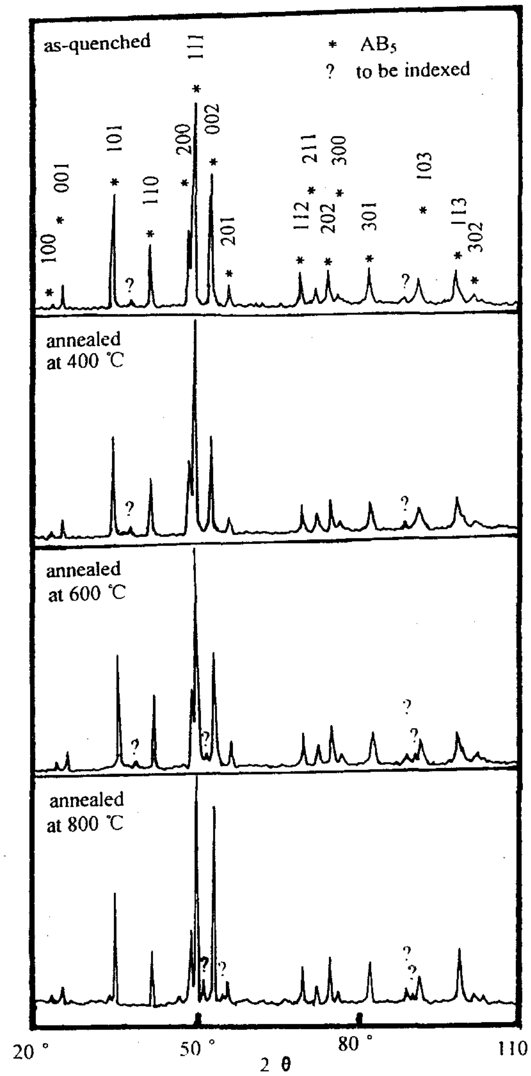

Fig. 6. XRD patterns for all samples under investigation.

taken as the growth of grains, together with the removal of defects in the crystals and disorder of the atoms.

The new phase mentioned above also exists in the master alloy [3]. Thus, it can be concluded that the phase is harmful to cycle durability. Further studies using SEM, TEM and EDAX techniques will be performed in an attempt to identify the phase and determine the characteristics of its distribution.

4. Conclusions

Annealing affects the capacity and discharge voltage, as well as the cycle life. Annealing can be used to raise the capacity at high discharge rates. At an appropriate temperature, annealing gives a promising alloy with large capacity, high discharge voltage and, especially, long-cycle durability. Annealing at too high a temperature (e.g., 800

°C) gives the largest discharge capacity but the worst durability. Annealing also flattens the discharge plateau region. The higher the annealing temperature, the larger the discharge capacity, the higher the discharge voltage and the flatter the discharge plateau. The same does not, however, produce any improvements in cycle life. New phases occur in the alloys annealed at 600 and 800 °C and these are responsible for the corresponding deterioration of cycle durability. Thus, annealing at a appropriate temperature is very effective for rapidly quenched alloys to serve as hydrogen-storage alloys with excellent synthetic properties.

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