Effect of Surface Modification by Heating in Argon on Charge/Discharge Characteristics of Mg_2Ni Electrode[†]

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Charge/discharge characteristics of Mg_2Ni electrodes were examined by focussing attention on the influence of surface modification by heating in argon. The initial activation was significantly easier for the electrodes heated at 550°C than un-heated ones. The surfaces of electrodes became porous by the heating because of the evaporation of magnesium. A MgO layer was formed during the heating. The improvement of charge/discharge characteristics by the heating was ascribed to the increase in the specific surface area and the porosity of the oxide film, and to the formation of MgNi_2 and nickel phases which should act as the local reaction sites for hydrogen during the charge and discharge processes.

(Received April 22, 1999; In Final Form June 15, 1999)

Keywords: Mg_2Ni , magnesium, surface property, initial activation, evaporation, oxidation, porous metal, electrode, nickel/metal hydride battery

I. Introduction

Magnesium and magnesium-based alloys are recognized as promising materials for the electrode of nickel/metal hydride battery because of their high hydrogen absorption capacities. In fact, it has been reported that discharge capacities of Mg-Ni-based alloys prepared by mechanical alloying are higher than theoretical discharge capacities of conventional hydrogen storage materials such as AB_5 type alloys⁽¹⁾⁻⁽⁶⁾. Their discharge capacities, however, decrease rapidly with increasing charge/discharge cycles⁽¹⁾⁻⁽⁶⁾. Lei *et al.*⁽¹⁾⁽²⁾⁽⁶⁾ attributed this rapid decrease to degradation in surface properties. The detailed surface analysis, however, has not been carried out.

In the previous papers, the present authors have reported charge/discharge characteristics of Mg_2Ni electrodes prepared by sintering in argon atmosphere⁽⁷⁾⁻⁽⁹⁾. The discharge capacities of electrodes sintered at 550°C kept an almost constant value up to 300 cycles, while that of un-sintered electrodes decreased promptly⁽⁷⁾⁽⁸⁾. Such significant improvement of the cyclic stability of discharge capacity was ascribed to the firm aggregation of powder particles caused by sintering and to the modification of surface states by heating in argon⁽⁷⁾⁽⁸⁾. The mechanism underlying the improvement of the cyclic stability, however, has not been fully clarified.

In the present study, the effect of surface modification by heating in argon on the charge/discharge characteristics of Mg_2Ni was examined. Sheet-type specimens were

used instead of the sintered specimens for detailed surface analysis. The surface state was examined with a scanning electron microscope (SEM) and an X-ray photoelectron spectrometer (XPS).

II. Experimental

Sheets of Mg_2Ni measuring $20 \times 15 \times 1 \text{ mm}^3$ were cut from an ingot prepared by melting. Their surfaces were polished with abrasive papers. Some specimens were heated in an argon flow at 0.1 MPa and 550°C for 90 min. The specimens in as-polished conditions are hereafter described as the specimen A and those heated in argon as the specimen B, respectively. Their lateral and back surfaces were covered with epoxy resin for avoiding disintegration of the specimens due to hydrogen absorption. The specimens were held in air at room temperature for 2 d to stiffen the resin.

Charge/discharge cycle tests were carried out with a conventional open cell filled with two electrodes and a 6 M KOH aqueous solution, where $\text{NiOOH}/\text{Ni}(\text{OH})_2$ was used for positive electrode. A charge/discharge cycle consisted of three steps: charging at 3 mA for 30 min, rest for 5 min and discharging at 3 mA. The charge and discharge currents per unit mass, 3 mA/g, were far smaller than those in the previous studies (80–100 mA/g and 20–25 mA/g)⁽⁷⁾⁽⁸⁾. This is because the specific surface areas of the sheets were considerably smaller than those of the sintered materials, whose specific surface areas ranged from 0.87 to 1.10 m^2/g ⁽⁷⁾⁽⁸⁾.

The specimen surfaces were observed with SEM. The concentration distributions of constituent elements were examined with energy dispersive X-ray spectroscopy (EDX). The chemical surface states were examined with XPS.

[†] This Paper was Presented at the Spring Meeting of the Japan Institute of Metals, held in Tokyo, on March 30, 1999.

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III. Results and Discussion

The variation of discharge efficiency with the cycle number is shown in **Fig. 1**. The discharge efficiency is defined here as the percentage of discharged quantity of electricity to charged one, where the latter was simply obtained as the product of charge current and time. In the case of the specimen A, the discharge efficiency increased gradually with cycle number; it took about 300 cycles to reach to 80%. On the other hand, the specimen B gave the 80% efficiency within 50 cycles. The initial activation markedly became easier by the heating in argon, even though the specimens were exposed to air for 2 d after the heating. Above 500 cycles, however, no significant difference was observed in the discharge efficiency between the specimens A and B; the difference in the initial surface state had no significant influence in this region. The specimen surfaces gradually cracked with the progression of charge/discharge cycles. The mechanism underlying the influence of the heating on the discharge characteristics is discussed later.

A typical example of SEM micrographs of the specimen A is shown in **Fig. 2(a)**. Second phase inclusions were observed. The concentration distribution of magnesium shown in **Fig. 2(b)** indicates magnesium enrichment in the inclusions. Therefore, the inclusions can be assigned to magnesium phase. A typical SEM micrograph of the specimen B is shown in **Fig. 3(a)**. There were holes in various shapes, whose sizes were comparable to those of the magnesium inclusions shown in **Fig. 2(a)**. These observations strongly suggest that the holes are formed by evaporation of the magnesium inclusions during the heating. Such selective evaporation of magnesium phase is due to its low melting point. An enlarged micrograph of the matrix part is shown in **Fig. 3(b)**. A large number of small holes measuring several hundreds nm were formed in the matrix Mg_2Ni . This can be ascribed to the selective evaporation of magnesium from the Mg_2Ni phase. It should be noted that this marked increase in the surface roughness due to the magnesium

Fig. 1 Variation of discharge efficiencies of specimens A and B with charge/discharge cycle.

Fig. 2 (a) Typical SEM micrograph of specimen A, (b) concentration distribution of magnesium in specimen A.

evaporation causes the increase in the specific surface area. The decrease in magnesium concentration in the matrix Mg_2Ni due to the evaporation should result in the formation of MgNi_2 and nickel phases.

Table 1 summarizes the surface compositions of the specimens determined by XPS. The concentration ratios of magnesium to nickel (Mg/Ni) were significantly higher than that in the bulk. Not only magnesium and nickel but also oxygen and carbon were observed. The concentration of carbon significantly decreased with the heating in argon, while no appreciable change was observed in the oxygen concentration. This suggests that the carbon was adsorbed on the top surface of an oxide film before the heating in argon and desorbed by the heating. The enrichment of magnesium at the surface can be ascribed to the selective oxidation of magnesium.

The photoelectron spectra of Mg 2p and O 1s are shown in **Fig. 4**. In the case of the specimen A, the Mg 2p peak was observed at 51.1 eV. According to the literature⁽¹⁰⁾, the binding energy of Mg 2p electrons of metallic magnesium (49.8 eV) shifts to 50.8 eV by oxidation to MgO. The binding energy of Mg 2p electrons in this figure is slightly higher than that of MgO. This should be due to $\text{Mg}(\text{OH})_2$ coexisting with MgO; the binding energy of Mg 2p electrons of $\text{Mg}(\text{OH})_2$ has been reported to be higher than that of MgO by 1 eV⁽¹¹⁾. The O 1s peak was observed at 532.5 eV. According to Peng and Barteau⁽¹⁰⁾ who examined adsorption behavior of H_2O on a mag-

(a)

(b)

Fig. 3 (a) Typical SEM micrograph of specimen B, (b) enlarged micrograph of matrix part.

Table 1 Surface compositions of specimens A and B.

Specimen	Concentration (at%)			
	Mg	Ni	O	C
A	20	2	38	40
B	39	2	43	16

nesium surface, the binding energy of O 1s electrons of MgO is 531.0 eV and that of hydroxyl is 533.1 eV. The binding energy shown in this figure is close to the latter, and no peak is observed around 531.0 eV. This suggests that a large amount of hydroxyl was adsorbed on the top surface of the oxide film. In the case of the specimen B, the Mg 2p peak was observed at 50.7 eV. This peak energy is slightly lower than that of the specimen A and close to the binding energy of corresponding photoelectrons from MgO (50.8 eV). In the O 1s spectrum of specimen B, a new peak was observed at 530.5 eV. This peak can be assigned to MgO. These results indicate that the thickness of MgO layer increased during the heating through the reaction with oxygen present in the argon gas as an impurity and the decomposition of $\text{Mg}(\text{OH})_2$ to MgO.

The modification of surface states caused by the heat-

Fig. 4 Spectra of Mg 2p and O 1s photoelectrons from specimens A and B.

ing in argon can be summarized as follows:

- (1) The specific surface area increased owing to the evaporation of magnesium;
- (2) The MgO layer was formed.

Taking these results into consideration, the mechanism underlying the improvement of the initial activation behavior can be proposed as follows. The increase in the specific surface area should result in the increase in the number of reaction sites for hydrogen. The formation of MgO would make the oxide film porous. This is because the molar volume of MgO is smaller than that of magnesium, and the magnesium surface could not be completely covered by MgO. According to Gregg and Jepson⁽¹²⁾ who examined oxidation behavior of magnesium, oxide films formed on magnesium are coherent and protective below 450°C, and the breakdown of the oxide films takes place above this temperature. They proposed that the oxide in the coherent films is in a metastable phase whose density is lower than that of the stable MgO, and that the breakdown of the coherent films is caused by the recrystallization to the stable MgO phase⁽¹²⁾. The nature of the metastable phase, however, has not been understood in detail. It is appropriate to consider that the surface of the specimen A is covered by this coherent oxide film which should act as the barrier to the dissolution of hydrogen in the specimen, and that this oxide film becomes porous by the heating in argon. Such increase in the porosity of oxide film should enable the electrolyte solution to contact with the substrate alloy directly. In addition to the increase in the specific surface area, the preferential evaporation of magnesium results in the formation of MgNi_2 and nickel phases as mentioned above. The oxide films formed on these phases would be reduced easily during the charge process compared with the oxide film on the Mg_2Ni phase since the free energy change for the formation of nickel oxide is far smaller than that of magnesium oxide. Hence, MgNi_2 and nickel phases are expected to act as the local reaction sites for hydrogen. It can therefore be concluded that the improvement of the initial activation behavior by the

heating in argon is due to the increase in the surface areas and the porosity of the oxide film, and to the formation of local reaction sites for hydrogen.

In the previous studies⁽⁷⁾⁽⁸⁾, it was revealed with X-ray diffraction analysis that $\text{Mg}(\text{OH})_2$ layer was formed on the sintered electrodes during the charge/discharge cycle tests. The formation of $\text{Mg}(\text{OH})_2$ layer should be one of the causes of the degradation of the electrodes. The growth rate $\text{Mg}(\text{OH})_2$ layer should decrease with local current density which decreases with increasing surface area and number of the reaction sites. For this reason, the cyclic stability of electrodes was improved by the sintering.

The difference in the discharge efficiency between the specimens A and B disappeared above 500 cycles as mentioned above. This can be interpreted as follows: the total area of new surfaces formed by the cracking became larger than the initial surface areas, and the fresh surfaces made a dominant contribution to the charge/discharge process in this region. No significant degradation in the discharge efficiency was observed up to 1000 cycles for both specimens A and B, while the degradation took place at about 300 cycles or less in the previous studies⁽⁷⁾⁽⁸⁾. This can be ascribed to the difference in the local current densities. The charge and discharge currents in the present study were far smaller than those in the previous studies⁽⁷⁾⁽⁸⁾ as mentioned above because the initial surface areas of the sheets were far smaller than those of sintered materials. The surface area of the sheets, however, increased with the cracking during the charge/discharge cycles. Therefore, it is plausible that the local current densities in the present study became lower than those in the previous studies⁽⁷⁾⁽⁸⁾.

IV. Conclusions

The heating in argon enabled the Mg_2Ni electrodes to be activated easily. The surface of Mg_2Ni sheet became

porous with the heating process owing to the evaporation of magnesium. The MgO layer was formed during the heating. The improvement of surface property by the heating was ascribed to the increase in the surface area and the porosity of the oxide film, and to the formation of MgNi_2 and nickel phases which should act as the local reaction sites for hydrogen during the charge/discharge cycles.

Acknowledgements

This work has been supported in part by a Grant-in-Aid for Scientific Research on Priority Areas A of "New Protium Function" from the Ministry of Education, Science, Sports and Culture. The authors are indebted for the gift of the positive electrodes to Human Environmental Systems Development Center of Matshushita Electric Industrial Co.

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