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Mg_2Ni 박막 전극의 전기화학적 특성에 미치는 열처리의 효과

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Effect of Heat Treatment of Mg_2Ni Thin Film Electrode on the Electrochemical Properties

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ABSTRACT

Ni/MH 박막전지의 전극으로 사용될 수 Mg_2Ni박막을 스퍼터링방법으로 제조하였다. Mg_2Ni합금박막은 Mg, Ni타겟을 이용하여 동시에 스퍼터링함으로서 제조하였다. KOH 액체전해질 및 $Ni(OH)_2$전극을 이용하여 전기화학실험을 하였다. Mg_2Ni 박막의 초기 싸이클 특성에 미치는 열처리 효과를 조사하기 위하여, 200 - 550℃로 변화시키면서 진공중에서 열처리를 하였다. 열처리온도가 300℃ 이하에서는 초기방전용량이 증가하였으며, 400℃ 열처리시에는 활성화시의 방전용량이 약 160mAh/g으로 가장 크게 나타났다.

주요기술용어 : Hydrogen storage alloy(수소저장합금), Mg_2Ni(마그네슘-니켈 합금), Thin film(박막), Microbattery(박막전지), Sputtering(스퍼터링), Heat treatment(열처리)

1. Introduction

Metal hydrides are promising materials for the hydrogen storage, chemical heat pump, hydrogen purification and Ni/MH(metal hydride) battery[1]. Especially, Ni/MH batteries have the large share of the rechargeable battery market[2]. There are a lot of metal hydrides such as $LaNi_5$ type, Mg_2Ni type, $Zr(Ti)Ni_2$ type and TiNi type alloys for the negative electrode material of Ni/MH batteries[3].

Thin film microbattery has been interested as a power source of MEMS(micro electromechanical system), intergrated circuits, and smart cards[4]. A lot of researches have been performed on the Li thin film batteries[4~9], but only a few papers were published on the metal hydride microbatteries[10~13]. Sakai et al.[10] reported that the maximum discharge capacities of $LaNi_5$ thin film electrode were

40mAh/g for the amorphous film, and 160mAh/g for crystalline film. The film prepared by R.F. sputtering under argon and hydrogen atmosphere. The solid electrolyte for microbattery were investigated such as tetramethylammonium hydroxide pentahydrate ($TMAOH_5$).

Kuriyama et al.[11] studied on the microcell such as $LaNi_{2.5}Co_{2.4}Al_{0.1}/TMAOH_5/NiOOH$(or MnO_2), and tested it up to 200 cycles. Sharp company also made the microbattery of $TiNi/Sb_2O_5nH_2O/MnO_2$. And, $LaNi_5$ thin film was fabricated by electron beam evaporation, and tested in a 6M KOH solution[12]. The crystalline film had a higher discharge capacity(250mAh/g) than amorphous film (160mAh/g) but had a lower capacity than the bulk alloy. The crystalline film peeled off the substrate when the film was thicker than 2500 angstroms. In the metal hydride thin film electrode, one of the severe problems was a low discharge capacity.

Magnesium based hydrogen storage alloys have great potential hydride electrode materials for Ni/MH batteries because of their high theoretical electrochemical capacity and low costl[3~18]. The bulk amorphous Mg_2Ni based electrode had a very high discharge capacity, but the capacity decay was very serious[13]. In addition, the crystalline Mg_2Ni based electrode showed a very low discharge capacity[14]. Most of researchers made a amorphous Mg_2Ni type alloy by a high-energy ball milling[15~17]. The melt-spin technique was also used[18]. The amorphous structure of the alloy can be easily obtained by sputtering at room temperature. Only a few researches have fabricated of Mg_2Ni type alloy thin film[19]. The thin were prepared by an RF-DC coupled magnetron sputtering. The composition ratio of Mg/Ni of the MgNix(x=0.56-1.19) could be controlled by target DC bias voltage. Recently, Lee et al reported the electrochemical properties of $Mg_{1-x}Ni_x$(x=0.33, 0.15, 0.10) film electrode[20]. However, there was no study on the effect of thermal treatement.

In this paper, we studied the effect of vacuum heat treatment of Mg_2Ni thin film electrode on the electrochemical properties.

2. Experimental

The Mg_2Ni thin films were deposited by DC magnetron co-sputtering using two different targets(pure nickel and magnesium). Fig. 1 showed the schematic diagram of DC magnetron sputter used in this experiment.

The copper sheet was used as the substrate material. The stainless steel deposition chamber was evacuated to 6×10^{-6}Torr prior to admitting high purity argon gas. The argon flow rate was 20 SCCM, and the distance

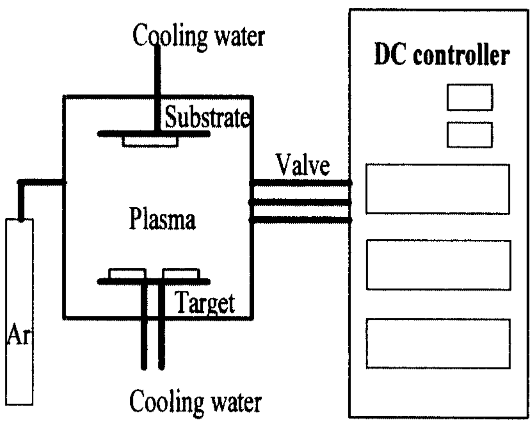


Fig. 1. Schematic diagram of DC magnetron sputtering system.

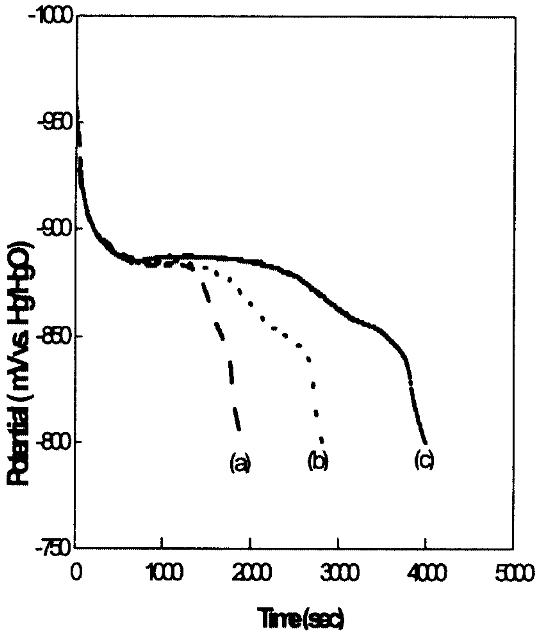


Fig. 2. The changes of discharge curves of an Mg_2Ni thin film electrode as a function of charge-discharge cycles. (a) 1st cycle, (b) 3rd cycle and (c) 10th cycle.

from the target to the substrate was about 16 cm. The Mg_2Ni film was deposited onto copper substrate at room temperature. The chemical composition was controlled by changing the ratio of electric power of each target(Mg and Ni). The thickness of the film was controlled by sputtering time and was about 0.5 µm. The surface and crystal structure was investigated using SEM(Scanning Electron Microscopy) and X-ray diffractometer, respectively. The electrochemical test of thin film electrode was conducted in a 6M KOH solution with Hg/HgO reference electrode and $Ni(OH)_2$ counter electrode. The cutoff voltage for discharge was 0.8V vs. Hg/HgO reference electrode. The thin film electrode was charged in a constant voltage 1.05V for 5h and then discharged in a constant current density of 100mA/g.

3. Results and Discussion

Fig. 2 showed the changes of the discharge curve of Mg_2Ni film electrode with charge-discharge cyclings. The discharge curves showed two plateau potential, the long upper discharge plateau(-0.9V) was followed by a shorter lower plateau(-0.87V). Two plateau potential regions might be related with two different reactions between Mg_2Ni film and hydrogen.

Fig. 3 represented the changes of discharge capacity of Mg_2Ni film electrode with cycling. The discharge capacity increased continuously as a function of number of cycles, and reached a maximum capacity of 120mAh/g at

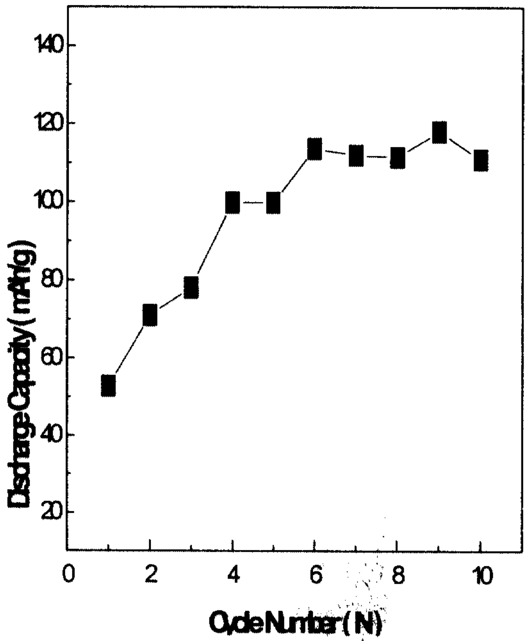


Fig. 3. The changes of discharge capacities an Mg_2Ni thin film electrode with cycles.

6th cycle. After 6cycles, the discharge capacity did not change, this behavior was similar to the activation behavior of metal hydride. The electrochemical test was performed in a 6M KOH solution with Hg/HgO reference electrode and $Ni(OH)_2$ counter electrode. The experimental condition of thin film electrode was similar as the bulk Mg_2Ni type electrode except using thin film type sample, but cycling behavior was different each other. Many papers have been published on the bulk Mg_2Ni based electrode[20~23]. The bulk amorphous electrode had one plateau potential (-0.8V) and lost 80 % of its maximum capacity within 10 cycles[20~23]. And also, it was reported that the degradation mechanism was related with oxidation of magnesium[15,22]. The initial cycling behavior was different from

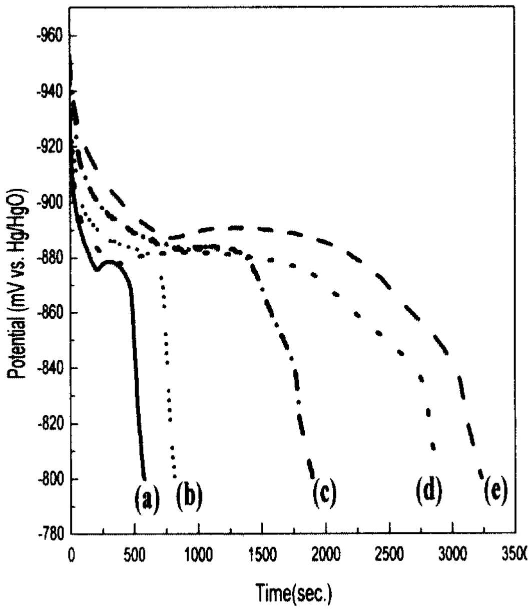


Fig. 4. Initial discharge curves of an Mg_2Ni thin film electrode as a function of heat treatment temperature in a vacuum. (a)400℃, (b)550℃, (c)before heat treatment, (d) 300℃, (e) 200℃.

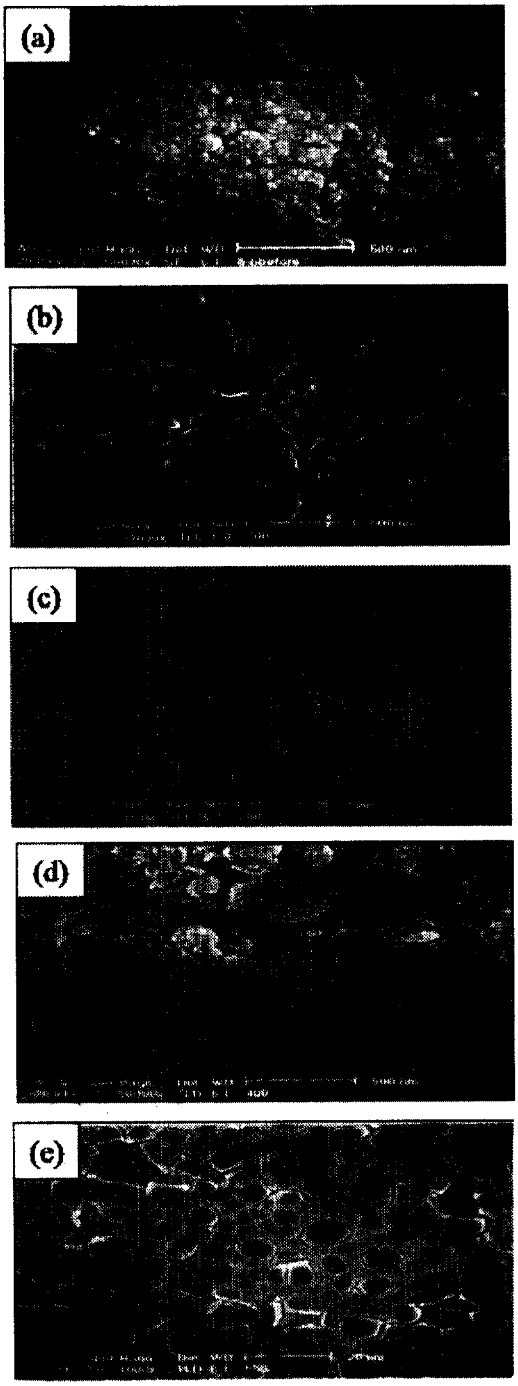


Fig. 5. SEM micrograph of Mg_2Ni thin film electrode after heat treatment. (a) Before heat treatment, (b) 200℃, (c) 300℃, (d) 400℃, (e) 550℃ (×50000).

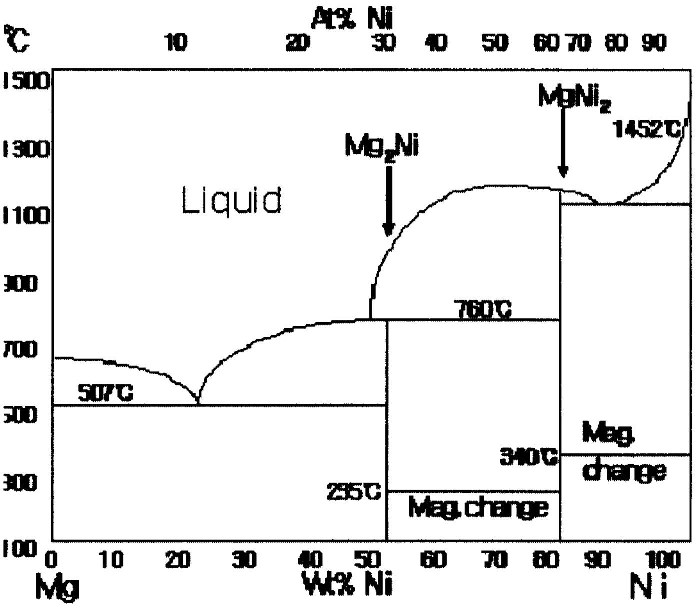


Fig. 6. Mg-Ni phase diagram.

thin film electrode. Providing a charge-discharge reaction occurs between Mg_2Ni and Mg_2NiH_4, the theoretical capacity of this alloy electrode is 963mAh/g. The maximum capacity was about 13% of theoretical value. This capacity was lower than the bulk Mg-Ni electrode prepared by mechanical alloying[13~15], but higher than any other amorphous thin film electrode[10~12].

The variations of the first discharge curve by vacuum heat treatment temperature were shown in Fig. 4. The discharge plateau potential did not change, but the discharge capacity increased by heat treatment below 300℃. Lee et al[20] reported that the Mg-Ni alloy thin film had the amorphous crystal structure. The increase of discharge capacity might be related with the crystallization of the amorphous structure. However, we could not find any traces of crystalline Mg_2Ni peaks from the XRD pattern of heat treated Mg_2Ni thin film. It is necessary to study further.

Fig. 5 represented the changes of SEM photographs by heat treatment temperatures. The original sample was consisted of the agglomeration of small spherical particles. After heat treatment, the surface of thin film was flatten. However, core structure was shown after 550℃ heat treatment.

The Mg-Ni phase diagram was represented in Fig. 6. The eutectic reaction between Mg and Mg_2Ni was occurred at 507℃. The core structure

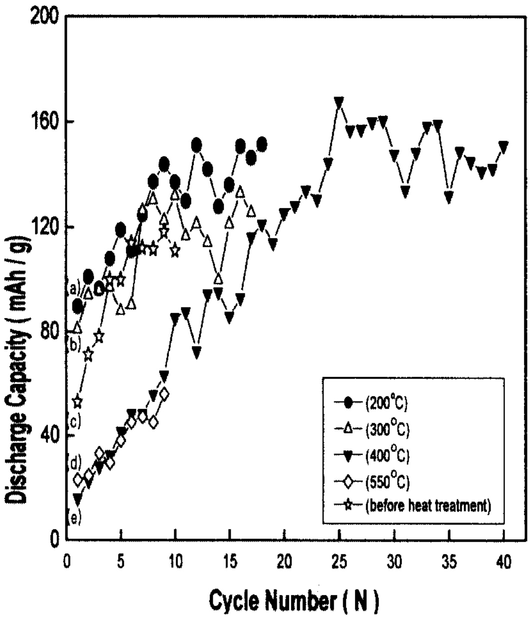
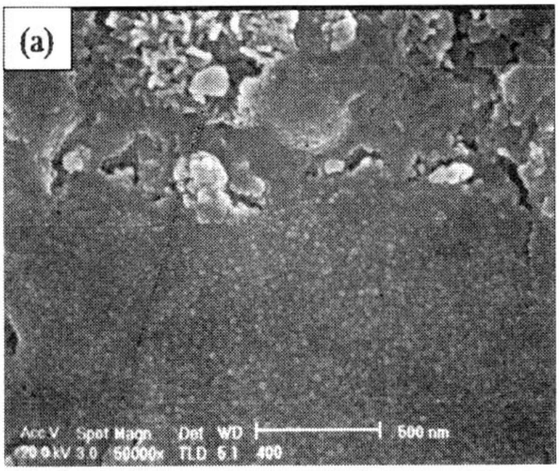


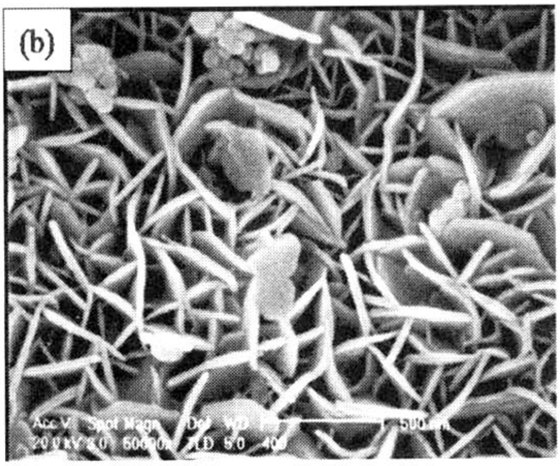
Fig. 7. Cycle characteristics of Mg_2Ni thin film electrode as a function of heat treatment temperature in a vacuum; (a)200℃, (b)300℃ (c)before heat treatment, (d)550℃, (e)400℃.

might be related with the eutectic reaction, which could be associated with the decrease of discharge capacity at 550°C heat treated sample.

Fig. 7 showed the variations of cycling properties of Mg_2Ni by heat treatment temperatures. The discharge capacities of all samples continuously increased by the number of cyclings. However, the cycled sample showed the disintegration between thin film electrode and substrate. After disintegration, the discharge capacity decreased drastically. The 400°C heat treated sample was disintegrated after cycles, which was higher than other samples. The adhesion property was improved by vaccum heat treatment. In general, the heat treatment of thin was good for adhesion. Especially, the 400°C heat treated sample represented the low first discharge capacity and long cycle life.



(a) before cycle test(×50000)



(b) after 40 cycle test(×50000)

Fig. 8. SEM micrograph of an 400℃ heat treated Mg_2Ni thin film electrode.

Fig. 8 showed the change of SEM photograph of an 400°C heat treated Mg_2Ni thin film electrode by cycling. The flat surface was changed to porous needle shape structure after 40 cycles. The porous needle shape had large surface area which could easily react with hydrogen. The shape change could be associated with the capacity increase by cycling. It is difficult to know the reason of shape change. It is necessary to study on this phenomena further.

4. Conclusion

The Mg_2Ni thin film was prepared by DC magnetron co-sputtering using Mg and Ni targets. we have studied on the effect of heat treatment of Mg_2Ni thin film electrode on the electrochemical properties. The discharge capacity of Mg_2Ni film increased continuously as a function of number of cycles. The surface morphology of the film was changed to needle type porous structure by cycling. The discharge capacity of Mg_2Ni thin film increased by vacuum heat treatment below 300°C. And also, we could obtain maximum capacity from the 400°C heat treated MgNi film.

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