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A Study on the Deposition Conditions of the TiNi Thin Film by DC Magnetron Sputtering

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DC 마그네트론 스퍼터링법에 의해 제조한 TiNi 박막의 증착조건에 관한 연구

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Abstract

In order to investigate the possibilities of microbatteries using TiNi type metal hydride, TiNi films were prepared by DC magnetron sputtering. The films were deposited under various Ar flow rates, DC powers and target-to-substrate distances to find the optimum sputtering conditions. The deposition rate of TiNi thin film increased by increasing the DC power and by decreasing the Ar flow rate and target-to-substrate distance. The chemical composition of the film changed as a target-to-substrate distance. The crystal structure of the film was amorphous state just after deposition and changed to crystalline by vacuum heat treatment.

초 록

수소저장합금 전극을 이용하는 박막전지의 제조를 위하여, TiNi 수소저장합금박막의 적정제조조건에 대하여 연구하였다. TiNi합금박막은 직류 스퍼터링을 이용하여 제조하였다. 증착변수인 아르곤유속, 타겥-기판거리, 직류 전력량등을 변화시키면서, 증착속도를 조사하였으며, Ti와 Ni의 화학조성비, 결정구조등을 조사하였다. 증착속도는 아르곤유속, 타겔-기판거리와 반비례하였으며, 직류전력량의 증가에는 정비례하여 증가하였다. 상온에서 증착후에는 비정질구조를 나타냈으나, 진공열처리 후에 결정질로 바뀌었다.

1. Introduction

Metal hydrides are promising materials for the hydrogen storage, chemical heat pump, hydrogen purification and Ni/MH battery[1]. Especially, Ni/MH batteries have been popular in the commercial market. There are many metal hydrides such as $LaNi_5$ type, Mg_2Ni type, $Zr(Ti)Ni_2$ type and TiNi type for the negative electrode material of Ni/MH batteries. Recently, microbatteries using thin film electrode have been interest as a power source of MEMS(micro electromechanical system) and smart cards[2]. A lot of researchers have been working on the Li ion microbatteries[2,3], but only a few papers were published in the field of MH microbatteries. Sakai et al[4] reported that the discharge capacities of $LaNi_5$ thin film electrode of amorphous and crystalline showed 40mAh/g, 160mAh/g, respectively. Kuriyama et al[5] made a 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. In the thin film type MH electrode, one of the severe problem was disintegration of the film during hydrogenation. TiNi alloy was a well known as shape memory alloy as well as hydrogen storage material. And also, TiNi alloy was not brittle but tough in mechanical properties. So TiNi thin film are considered as a potential electrode material for Ni/MH microbatteries. Only a few papers have been published in the fabrication of TiNi thin film[6,7], and there was no paper on the deposition rates as the sputtering conditions.

In this paper, we studied the fabrication conditions of TiNi thin film using DC magnetron sputter and the electrochemical properties of TiNi electrode.

2. Experimental

The TiNi thin films were deposited by DC magnetron sputtering. The $Ti_{60}Ni_{40}$ target was made by VIM(vacuum induction melting). The diameter of target is 2 inch. The stainless steel and glass sheet was used as the substrate. The ultimate and the deposition pressure were 5×10^{-6}Torr and 1~6 mTorr, respectively. In order to obtain the optimum sputtering condition for TiNi thin film, we have changed the Ar flow rates(1~12 sccm), the distances between target and substrate (10~23㎝), DC power(50~250watt). For the crystallization of thin film, the vacuum heat treatments were performed from 600 to 800℃. The electrochemical test of TiNi thin film electrode were conducted in a 6M KOH solution with Hg/HgO reference electrode, Pt counter electrode. The cutoff voltage on charge 3.0V and for discharge was 0.5V vs Hg/HgO reference electrode. TiNi thin film electrode was charged in a current density of 0.032mA/㎠ and 0.016mA/㎠ for discharge. In order to comparison with thin film type electrodes, TiNi powder electrodes were prepared using mixed powder of TiNi and Ni in a weight ratio of 1:3. And, it was cold pressed with a compacting pressure of 5 tons/㎠, and then wrapped in the Ni mesh as a current collector. TiNi powder electrode was charged in a current density of 100mA/g and 200mA/g for discharge. For the study on the deposition rate of thin film, the thickness of film was measured by a-step. The crystal structure was investigated using X-ray diffractometer. The chemical composition of film was characterized by EDS(Energy Dispersive Spectroscopy) analysis.

3. Results

Fig. 1 shows the changes of deposition rate as a function of the distance between target and substrate. The sputtering was performed for 1hr under 100Watt DC power, 4sccm Ar flow rate. The deposition rate increased as decreasing the target-to-substrate distance.

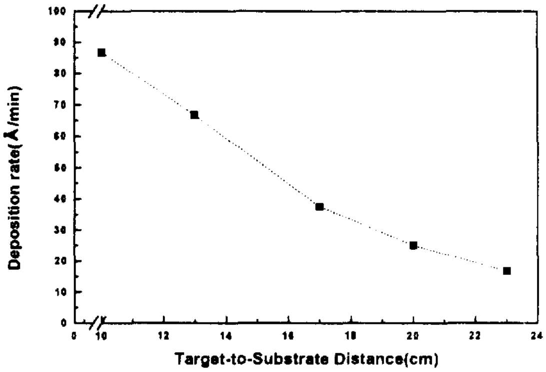

Fig. 1 The changes of deposition rate with Target-to-Substrate distance for the TiNi film prepared under the 100Watt DC power, 4sccm Ar flow rate.

Fig. 2 shows the change of Nickel concentration in Ti1-xNix film with the target-to-substrate distance. The chemical composition of TiNi changed with the target-to-substrate distance. The $Ti_{49.7}Ni_{50.3}$ film could be obtained in the 17cm target-substrate distance. This was similar as the Carchano's result that the composition of TiNi film changed as a function of product of deposition pressure and target-to-substance distance[8]. This might be related with the loss of the elementary species during transport from the target to the substrate.

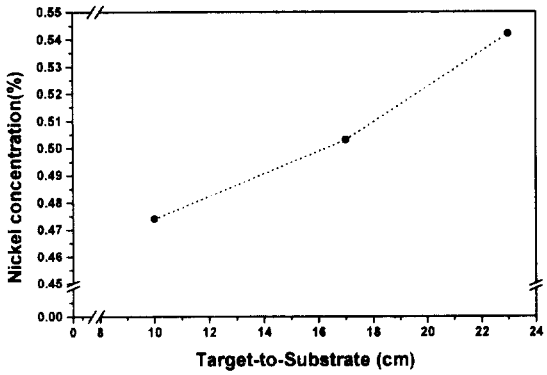

Fig. 2 The change of Nickel concentration in $Ti_{1-x}Nix$ film as a function of target-to-substrate distance.

Fig. 3 represents the changes of the X-ray diffraction patterns of the TiNi thin film by vacuum heat treatments. The film was deposited for 1hr under 10cm target-to-substrate distance, 200Watt DC power and 12 sccm Ar flow rate. For the as deposited TiNi film at room temperature, there was no sharp diffraction peak. The film would be amorphous structure. The crystallization behavior could be showed above 600°C heat treatment in a vacuum. After 800℃ vacuum heat treatment, the film represented the Ti_2Ni crystalline structure.

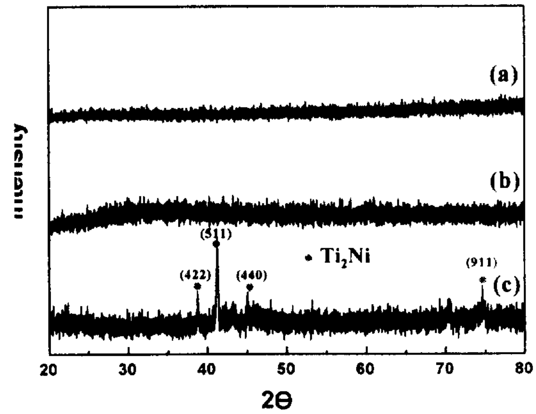

Fig. 3 The effect of vacuum heat treatment on the crystal structure of TiNi thin film
(a) as deposition at room temperature
(b) vacuum heat treatment at 600℃ for 0.5hr
(c) vacuum heat treatment at 800℃ for 1hr

Fig. 4 shows the SEM result of TiNi film deposited on the stainless steel substrate. There was no special phase on the surface.

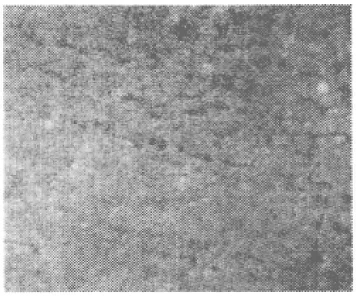

Fig. 4 The SEM morphology of TiNi thin film deposited on the stainless steel sheet substrate

In order to obtain optimum sputtering condition, TiNi film were prepared under various Ar flow rates and DC powers. The effect of Ar flow rates on the deposition rate are shown in Fig. 5. The film was prepared for 1hr under the 10cm target-to-substrate distance and 100Watt DC power. The deposition rate decreased as increasing the Ar flow rate.

Fig. 6 represents the changes of deposition rates as a DC power. The deposition rate increased as increasing DC power. The maximum rate of 297Å/min was obtained at the highest DC power, 250Watt and 10cm target-to-substrate distance. This phenomena might be related with the changes of sputtering yield as a power.

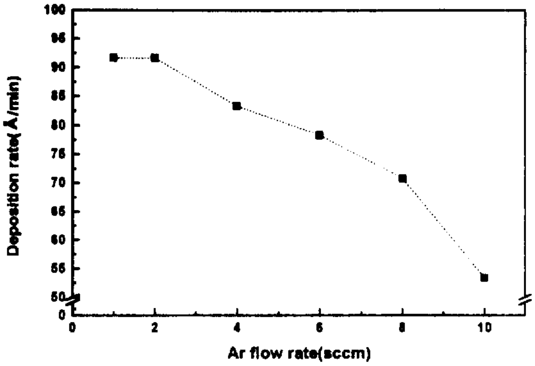

Fig. 5 The variations of deposition rate as a function of Ar flow rate for the TiNi film prepared under the 10cm target-to-substrate distance and 100Watt DC power.

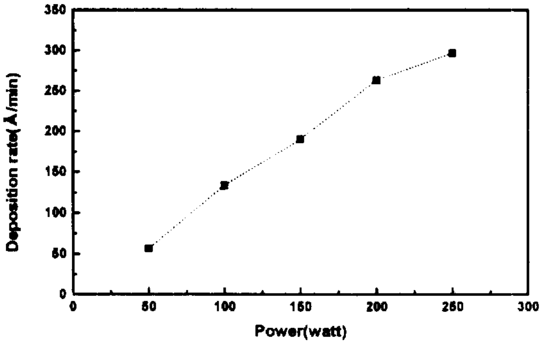

Fig. 6 The change of deposition rate as a function of DC power for the TiNi film prepared under the 2sccm Ar flow rate and 10cm target-to-substrate distance.

We have studied the electrochemical properties of Ti-Ni thin film. However, we could not find any charge - discharge behavior in the cell of Pt/6M KOH/Ti-Ni film. In order to investigate the electrochemical properties of Ti-Ni alloy, the TiNi electrode made by TiNi powder. Fig. 7 showed the 1st discharge curve of TiNi powder electrode. The discharge capacity was 63mAh/g, which was relatively low. Fig. 8 represented the initial cycle test results. The capacity increased to 87mAh/g as increasing the cycle number. Although the capacity of TiNi powder electrode was very low, it represented a typical metal hydride electrode behavior. So, it is necessary to study further for TiNi thin film electrode.

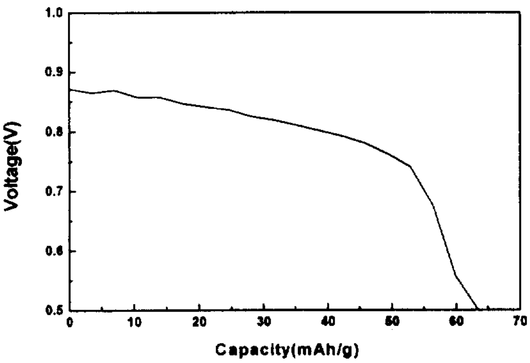

Fig. 7 The 1st discharge curve of TiNi powder electrodes.

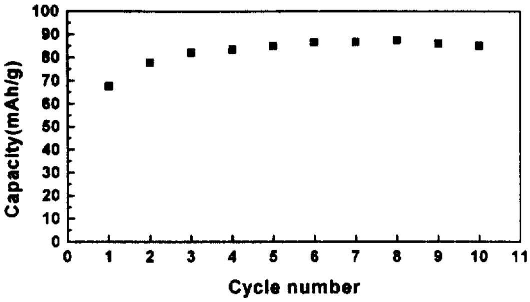

Fig. 8 The effect of charge-discharge cyclings of TiNi powder electrode on the discharge capacities.

4. Conclusion

1. The deposition rate of TiNi thin film increased by increasing the DC power and by decreasing the Ar flow rate and target-to-substrate distance. The maximum deposition rate 297Å/min, were obtained at 250Watt DC power.

2. The crystal structure of as deposited film was amorphous state, and changed to Ti_2Ni crystalline structure under vacuum heat treatment at 800℃. The nickel chemical composition of $Ti_{1-x}Ni_x$ was changed by sputtering condition, $Ti_{49.7}Ni_{50.3}$ were obtained at 17cm target-to-substrate.

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