Journal of Alloys and Compounds 330–332 (2002) 597–600

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Charge–discharge characteristics of $TiV_{2.1}Ni_{0.3}$ alloy surface-modified by ball-milling with Ni or Raney Ni

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Abstract

For the purpose of improving the charge–discharge characteristics of the $TiV_{2.1}Ni_{0.3}$ alloy, it was surface-modified by ball-milling with Ni and Raney Ni which worked as a catalyst for hydriding and dehydriding. The surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni decreased the maximum discharge capacity, but the cycle durability was greatly improved. On the other hand, the surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Raney Ni improved both the discharge capacity and cycle durability. The surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni and Raney Ni suppressed the positive shift of the plateau potential in the discharge curve and the negative shift of the rest potential. In particular, Ni was more effective than Raney Ni. The high-rate dischargeability was improved by surface modification with Raney Ni.

Keywords: V-based hydrogen storage alloy; Bcc; Nickel–metal hydride battery; Mutual diffusion layer; Ball-milling

1. Introduction

V-based alloys with body-centered cubic (bcc) structure are promising as negative electrode materials for nickel–metal hydride batteries and hydrogen storage materials for fuel cells because of their high capacity per volume. Several papers have been reported on the charge–discharge characteristics of the V-based alloys [1–4]. Recently, it has been found by our group that the $TiV_{2.1}Ni_{0.3}$ alloy with the BCC structure as a main phase showed high hydrogen storage capacity in pressure–composition isotherm measurement and high discharge capacity in charge–discharge tests [5,6]. However, it showed poor cycle performance probably due to the dissolution of the alloy components in a 6 M KOH solution.

In this study, the surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy by ball-milling with Ni or Raney Ni is performed and the effect of the ball-milling on the charge–discharge characteristics is investigated. In our previous papers [7,8], the surface modification of the alloy by ball-milling it with amorphous MgNi was useful for suppressing the deterioration of the $TiV_{2.1}Ni_{0.3}$ alloy. Ni has been well-known to be an effective catalyst for electrochemical and chemical hydriding and dehydriding, and Raney Ni has much higher catalytic activity than Ni. So, the ball-milling of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni and Raney Ni would be expected to be effective for improving not only the deterioration but also rate-capability.

2. Experimental

The $TiV_{2.1}Ni_{0.3}$ powder was prepared according to the previous paper [6]. The resulting powder was sieved to different particle sizes with less than 25 μm for X-ray diffractometry (XRD) and 25–106 μm for surface modification.

The Ni powder of 99.99% (Aldrich) for the surface modification of $TiV_{2.1}Ni_{0.3}$ alloy was used as received. On the other hand, the Raney Ni powder was made from the Raney Ni alloy powder (Ni content, ca. 50%, Wako Pure Chemical) according to Ref. [9].

The mixture of the $TiV_{2.1}Ni_{0.3}$ alloy with 30 wt.% Ni powder or Raney Ni was put in a stainless steel pot and ball-milled at a rotating speed of 180 rpm for 3 h to prepare $TiV_{2.1}Ni_{0.3}$–M (M=Ni or Raney Ni) composite.

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0925-8388/02/$ – see front matter
PII: S0925-8388(01)01543-2

The surface modification was carried out in an argon atmosphere.

XRD measurements of the $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composites were carried out using an X-ray diffractometer (Cu Kα/λ=1.541 Å, 40 kV, 20 mA).

The pellet-type negative electrode used for electrochemical measurements was prepared in the same procedure as the previous paper [6]. The electrolyte solution was 6 M KOH aqueous solution and a positive electrode was a NiOOH/$Ni(OH)_2$ electrode. In the charge–discharge cycle measurements the negative electrode was charged at 100 mA g^{-1} for 8 h and discharged at 50 mA g^{-1} to the cut-off potential of −0.75 V versus Hg/HgO. After each charging, the circuit was opened for 10 min. The electrochemical measurements were carried out at 30°C.

3. Results and discussion

In XRD patterns of the $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composites, peaks assigned to the body-centered cubic (bcc) main phase of the $TiV_{2.1}Ni_{0.3}$ alloy and Ni or Raney Ni were observed. The ball-milling with Ni or Raney Ni powder did not influence the XRD peaks for the bcc main phase, suggesting that the ball-milling influenced not the bulk structure of the $TiV_{2.1}Ni_{0.3}$ alloy but the surface structure.

Fig. 1 shows the discharge capacity as a function of cycle number for the $TiV_{2.1}Ni_{0.3}$ alloy electrode and the $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composite electrodes. As can be seen from this figure, the $TiV_{2.1}Ni_{0.3}$ electrode showed the maximum discharge capacity of 470 mAh g^{-1} at the first cycle. The surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni or Raney Ni did not significantly influence the initial activation characteristics. The surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni decreased the maximum discharge capacity, while that with Raney Ni increased up to 495 mAh g^{-1}. The cycle durability of the discharge capacity was improved more or less by the surface modification. In particular, the surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni showed a marked effect. These results clearly indicate that the surface modification is meaningful for improving the charge–discharge properties of the $TiV_{2.1}Ni_{0.3}$ alloy.

Fig. 2 shows discharge curves at the first, second, fifth, 10th and 20th charge–discharge cycles of the $TiV_{2.1}Ni_{0.3}$ alloy electrode and $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composite electrodes. As can be seen from Fig. 1, the $TiV_{2.1}Ni_{0.3}$ electrode showed poor cycle durability. The plateau potential at first cycle of the $TiV_{2.1}Ni_{0.3}$ electrode was about −0.85 V versus Hg/HgO and this potential gradually shifted to the positive direction with an increase in cycle number, suggesting the deterioration of the electrode. On the other hand, the surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni and Raney Ni suppressed the

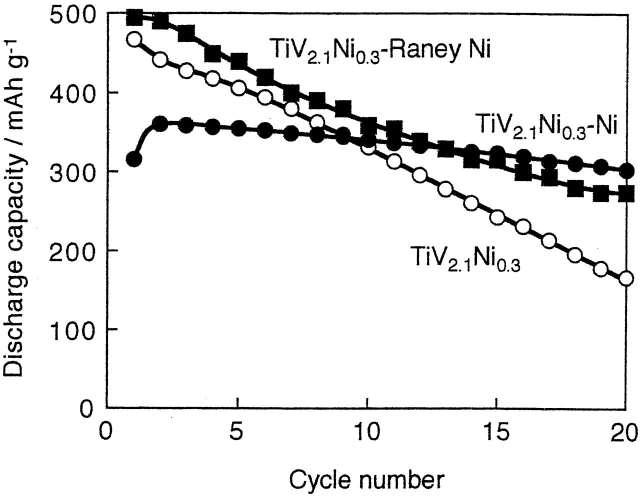

Fig. 1. Discharge capacities as a function of cycle number for $TiV_{2.1}Ni_{0.3}$ alloy electrode and $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composite electrodes.

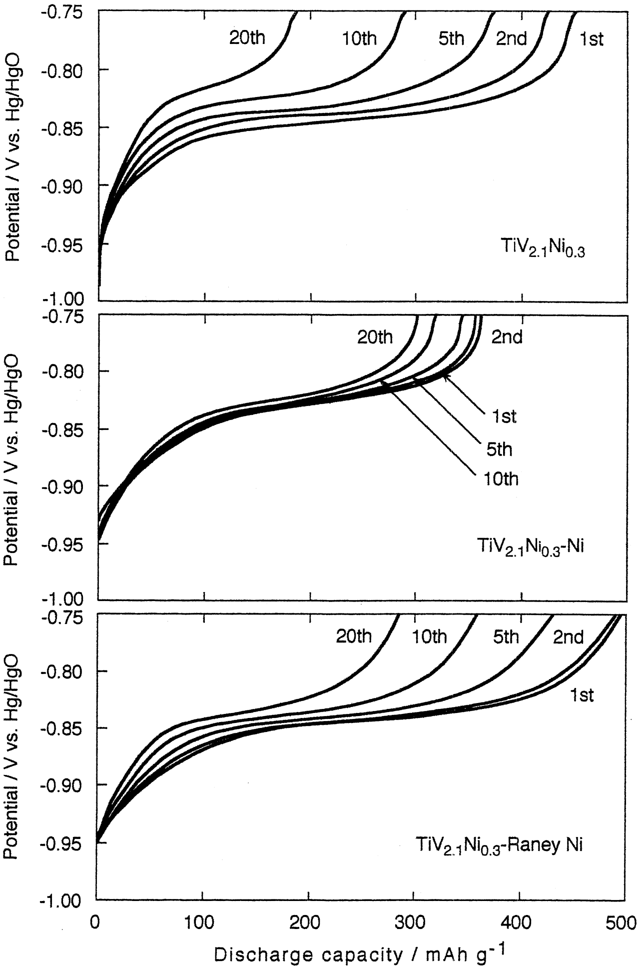

Fig. 2. Discharge curves at first, second, fifth, 10th and 20th charge–discharge cycles of $TiV_{2.1}Ni_{0.3}$ alloy electrode and $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composite electrodes.

positive shift of the potential and, in particular, Ni was more effective for the surface modification than Raney Ni. It has been reported in our previous papers [7,8] that the cycle durability of the $TiV_{2.1}Ni_{0.3}$ alloy was improved by ball-milling of the $TiV_{2.1}Ni_{0.3}$ alloy with MgNi alloy due to the formation of the mutual diffusion layer in the interface region between the $TiV_{2.1}Ni_{0.3}$ and MgNi alloys. In the present case, it was found by X-ray photoelectron spectroscopy that the mutual diffusion layer, which can work as a barrier to the corrosion, was formed in the interface region between the $TiV_{2.1}Ni_{0.3}$ alloy and Ni or Raney Ni.

Fig. 3 shows time course of the rest potential for the $TiV_{2.1}Ni_{0.3}$ alloy electrode and $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composite electrodes immersed in a 6 M KOH solution. In the case of the $TiV_{2.1}Ni_{0.3}$ alloy, the rest potential negatively shifted with an increase in immersion time due to the hydrogen absorption with the corrosion of the alloy in the local-cell mechanism [10]. The change in the rest potential was greatly retarded by the surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni or Raney Ni. In particular, Ni was more effective for suppression of the negative potential shift than Raney Ni. These results clearly indicate the usefulness of the surface modification by ball-milling with Ni and Raney Ni.

Fig. 4 shows the high-rate dischargeability (HRD) of the $TiV_{2.1}Ni_{0.3}$ alloy electrode and $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composite electrodes. In this figure, HRD is defined as the percentage of the discharge capacity at various current density to that at 25 mA g^{-1} and the HRD value at 25 mA g^{-1} in each case is 100%. The surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Raney Ni showed higher HRD value than the alloy, whereas that with Ni was not effective. The mutual diffusion layer formed by ball-milling with Ni can suppress the contact with the electrolyte solution effectively. Therefore, not only the corrosion but also the following discharge reaction at the negative electrode can be suppressed.

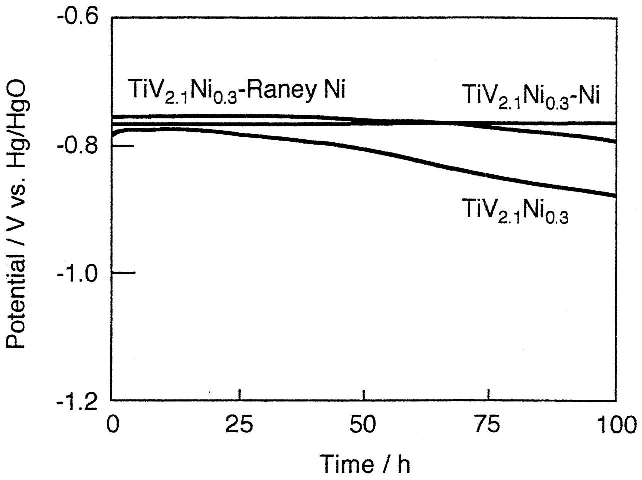

Fig. 3. Time courses of rest potential for $TiV_{2.1}Ni_{0.3}$ alloy electrode and $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composite electrodes immersed in a 6 M KOH solution.

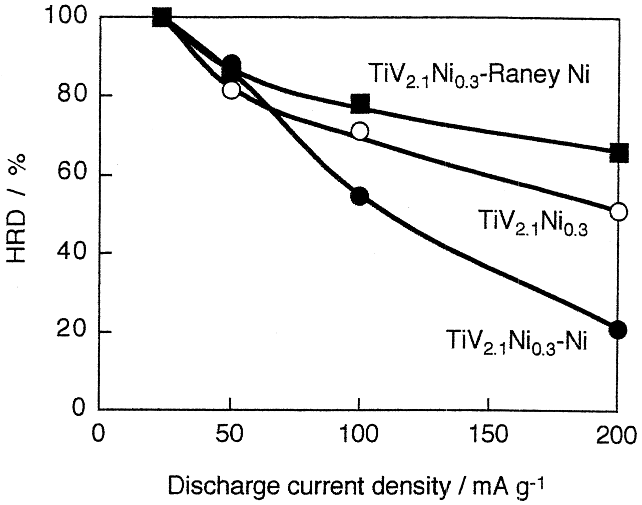

Fig. 4. High-rate dischargeability (HRD) of $TiV_{2.1}Ni_{0.3}$ alloy electrode and $TiV_{2.1}Ni_{0.3}$–M (M=Ni and Raney Ni) composite electrodes. HRD is defined in the text.

$$MH + OH^- \rightarrow M + H_2O + e^- \quad (1)$$

where M represents an alloy. This must cause the lowering of the high-rate dischargeability.

4. Conclusions

The results obtained in this work are summarized as follows.

1. The ball-milling influenced not the bulk structure of the $TiV_{2.1}Ni_{0.3}$ alloy but the surface structure.
2. The surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni decreased the maximum discharge capacity, but the cycle durability was greatly improved, while that with Raney Ni increased up to 495 mAh g^{-1} and the cycle durability was also improved.
3. The surface modification of the $TiV_{2.1}Ni_{0.3}$ alloy with Ni and Raney Ni suppressed the positive shift of the plateau potential and the negative shift of the rest potential. In particular, Ni was more effective than Raney Ni, indicating clearly the usefulness of the surface modification by ball-milling with Ni and Raney Ni.
4. High-rate dischargeability was improved by ball-milling with Raney Ni.

Acknowledgements

This work has been partially supported by a Grant-in-Aid for Scientific Research on Priority Areas (A) of ‘New

Protium Function' (No. 10148105) and Scientific Research on Priority Areas (B) of 'Ionics Devices' (No.11229205) from the Ministry of Education, Science, Sports and Culture of Japan.

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