

On the elemental substitutions of titanium-based hydrogen-storage alloy electrodes for rechargeable Ni–MH batteries

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Partial substitutions of nickel in Ti_2Ni intermetallic compound with cobalt, potassium, boron and aluminium have been studied in the present paper. It is found that cobalt and boron additions are beneficial but aluminium addition is detrimental to the specific capacity of the electrode. Potassium does not have any significant effect on the specific capacity of the electrode from our work. Cobalt, potassium and aluminium additions are all found effective in increasing the cycle life of Ti_2Ni electrode, although by different mechanisms.

1. Introduction

Many efforts have been made by the present authors and other researchers to improve the performance of titanium-based hydrogen-storage alloy electrodes for rechargeable Ni–MH batteries [1–6] recently. Approaches such as surface modification of alloy powder, combination of Ti_2Ni and $TiNi$ alloys and also elemental substitutions have been successful in improving the specific capacity and in particular the cycle life of the Ti_2Ni alloy electrode. Although Ti_2Ni is characterized as having a high theoretical specific capacity, the practical specific capacity is much lower and, in particular, its cycle life is rather short, which retards the commercialization of this promising material. To facilitate the performance of Ti_2Ni alloy electrode, elemental substitutions of nickel using cobalt, potassium, boron and aluminium are studied systematically in the present paper. The reasons for using Co, K–B and Al as substituents are described as follows. Cobalt is characterized as having similar electron configurations ($(3d^7(4s)^2)$) to nickel ($(3d^8(4s)^2)$), a similar but slightly larger atomic radius (Co, 1.47 Å; Ni, 1.42 Å) and a similar but slightly larger atomic volume (Co, $6.7 \text{ cm}^3 \text{ mol}^{-1}$; Ni, $6.59 \text{ cm}^3 \text{ mol}^{-1}$). Potassium is known as one of the most active elements with a negative electrode potential. The added potassium might act as a “micro-anode” to be sacrificed and the bulk hydrogen storage alloy which might therefore act as a “micro-cathode” may be protected. Because of the commonly known difficulty of potassium addition, the starting material for potassium addition in the present work is potassium borohydride. Therefore addition of boron together with potassium is inevitable. As for aluminium, it is lighter and cheaper than most metals and is characterized as having good passivity under some

circumstances. It was used to increase the cycle life of rare-earth system hydrogen storage alloy electrodes and is therefore expected to have the same behaviour for the titanium system.

2. Experimental procedure

Alloys of various nominal compositions were made by vacuum arc melting under argon protection. Additional amounts of boron were added to a precursor alloy, namely, $Ti_2Ni_{0.99}(KB)_{0.01}$, to take into account the possible elemental interactions of B and K. The starting materials for the synthesis of different alloys investigated were Ti (99.9 wt %), Ni (99.9 wt %), Co (99.9 wt %), Al (99.9 wt %), B (99.9 wt %) and KBH_4 (99.9 wt %). All the materials were provided by Aldrich Chemical Company Pty. Care was taken to avoid any metal evaporation. Homogeneity was ensured by repeated turning and melting of the alloy ingot five times. The alloy ingots were consequently crushed and ground into powders of below 100 mesh. Each fine powder was then mixed with 10 wt % polyvinyl alcohol solution in the ratio of 10:1. The mixed powder was then cast onto a foam nickel sheet. The pasted foam nickel sheet was then, when dry, pressed at a pressure of 15 kN cm^{-2} to form a hydrogen storage alloy electrode.

Charge–discharge cycles were completed using a DEC-1 automatic charge–discharge unit and data collected with a Macintosh Performer 400 interfaced with a MacLab-8. A Hg/HgO reference electrode and a nickel foil auxiliary were employed. The hydrogen storage alloy electrodes were charged to gassing voltage followed by a rest period of 30 min and were then deeply discharged galvanostatically at a current density of 20 mA cm^{-2} to 0.70 V versus

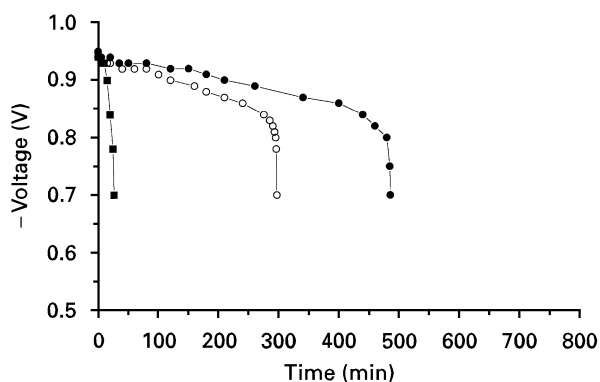


Figure 1 Discharge curves of pure Ti_2Ni alloy electrode. (●), cycle 1; (○), cycle 2, (■), cycle 3.

Hg/HgO. The electrolyte used was 6 M KOH aqueous solution.

“Steady-state” anodic potentiostatic polarization curves were obtained using an AMEL model 553 potentiostat in a 6 M KOH aqueous solution. A platinum mesh auxiliary electrode and a Hg/HgO reference electrode were employed.

X-ray diffraction (XRD) analysis was carried out using a Philip PW1010 X-ray diffraction unit with TRACES software.

Scanning electron microscopy (SEM) analysis was performed using a Leica/Cambridge Stereoscan 440.

3. Results and discussion

The discharge curves of the electrode fabricated from pure Ti_2Ni alloy are given in Fig. 1. It can be clearly seen that the electrode is not capable of being further discharged after only 3 cycles. The influences of cobalt, potassium–boron and aluminium additions on the charge-discharge performance of the electrodes are described as follows.

3.1. Cobalt addition

Cobalt-added alloys with the formula $\text{Ti}_2\text{Ni}_{1-x}\text{Co}_x$ were made with x values of 0.02, 0.05, 0.2 and 0.4. The discharge curves of the electrode fabricated from $\text{Ti}_2\text{Ni}_{0.98}\text{Co}_{0.02}$ are given as an example of cobalt-added electrodes in Fig. 2. By comparing Figs 1 and 2 it can be clearly seen that the performance of the Ti_2Ni electrode is greatly increased on cobalt addition. An additional comparison of the electrode performance is given in Fig. 3 in terms of capacity-decay curves. To demonstrate further the effect of cobalt

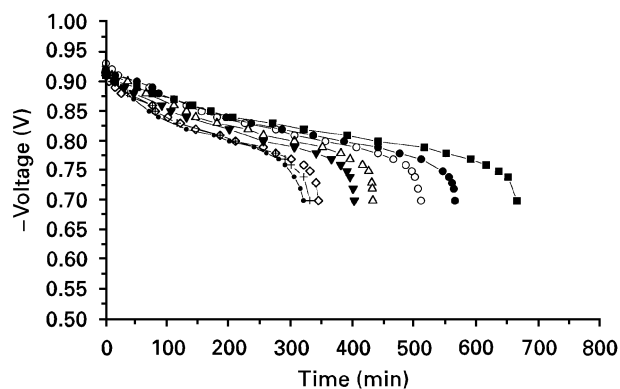


Figure 2 Discharge curves of $\text{Ti}_2\text{Ni}_{0.98}\text{Co}_{0.02}$ electrode. (■), cycle 1; (●), cycle 2; (○), cycle 3; (△), cycle 4; (▼), cycle 5; (◇), cycle 6; (+), cycle 7; (●), cycle 8.

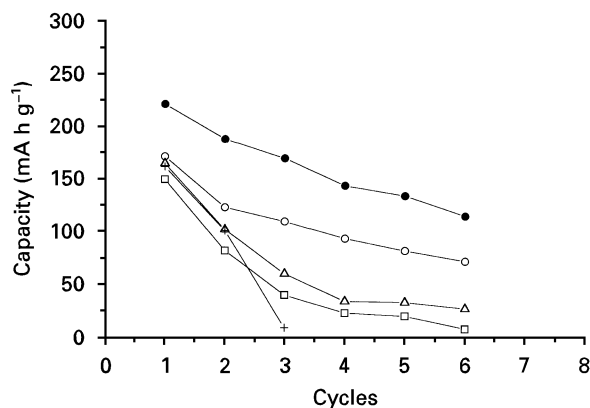


Figure 3 Capacity decay curves of electrodes with different cobalt contents. (●), $\text{Ti}_2\text{Ni}_{0.98}\text{Co}_{0.02}$; (○), $\text{Ti}_2\text{Ni}_{0.95}\text{Co}_{0.05}$; (△), $\text{Ti}_2\text{Ni}_{0.8}\text{Co}_{0.2}$; (□), $\text{Ti}_2\text{Ni}_{0.6}\text{Co}_{0.4}$; (+), Ti_2Ni .

addition on the capacity decay of Ti_2Ni electrodes, the percentage of capacity retention of the electrodes at various cycles is given in Table I, while the relationship between the specific capacity during the first three cycles and the corresponding cobalt content is illustrated in Fig. 4. The data in Table I and Fig. 4 show that the capacity retention of the electrodes containing cobalt is much higher than that of the pure Ti_2Ni electrode at each given cycle (the specific capacity of the first cycle is the initial capacity value of each corresponding electrode and, therefore, the capacity retention in the first cycle is 1 for each electrode). For example, the percentage of capacity retention of a $\text{Ti}_2\text{Ni}_{0.98}\text{Co}_{0.02}$ electrode after 3 cycles is 77% while that of the Ti_2Ni electrode is only about 6%. This

TABLE I Percentage of capacity retention of electrodes with different cobalt contents at different cycles

Electrode	Capacity retention (%)					
	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
Ti_2Ni	1.00	0.62	0.06			
$\text{Ti}_2\text{Ni}_{0.98}\text{Co}_{0.02}$	1.00	0.85	0.77	0.65	0.60	0.52
$\text{Ti}_2\text{Ni}_{0.95}\text{Co}_{0.05}$	1.00	0.72	0.64	0.54	0.48	0.42
$\text{Ti}_2\text{Ni}_{0.8}\text{Co}_{0.2}$	1.00	0.62	0.37	0.26	0.20	0.16
$\text{Ti}_2\text{Ni}_{0.6}\text{Co}_{0.4}$	1.00	0.55	0.27	0.16	0.13	0.05

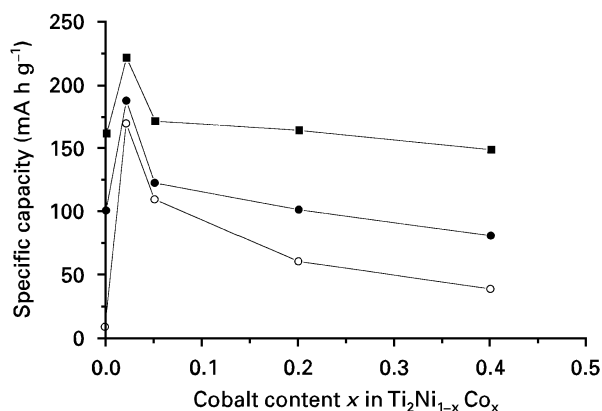


Figure 4 Capacity variation of electrodes with different cobalt contents during the first 3 cycles. (■), cycle 1; (●), cycle 2; (○), cycle 3.

clearly indicates that cobalt is very effective in lengthening the cycle life of the Ti_2Ni electrode. The reason for this may be that cobalt addition enlarges the lattice cell and hence reduces the lattice expansion and contraction during the corresponding hydriding and dehydriding processes, i.e., powder disintegration is slowed down. SEM studies of the morphology provide direct evidence of the effect of cobalt addition of reducing the rate of powder disintegration, as shown in Figs 5 and 6. It can be seen that the alloy without cobalt addition has disintegrated severely after only 3 cycles (Fig. 5), whereas the alloy powder with a cobalt content of 0.67 at % ($\text{Ti}_2\text{Ni}_{0.98}\text{Co}_{0.02}$) is only slightly degraded, even up to 8 (deep) cycles (Fig. 6).

Among the electrodes with different cobalt additions, the $\text{Ti}_2\text{Ni}_{0.98}\text{Co}_{0.02}$ electrode has the most significant effect (Figs 3 and 4). The variation in electrode specific capacity at different numbers of cycles versus cobalt content is displayed in Fig. 4. With only 0.67 at % (i.e., 0.02 in $\text{Ti}_2\text{Ni}_{0.98}\text{Co}_{0.02}$) cobalt, the specific capacity of Ti_2Ni is greatly increased. However, with further increase in cobalt up to 13.33 at % (i.e., 0.4 in $\text{Ti}_2\text{Ni}_{0.6}\text{Co}_{0.4}$), the specific capacity decreases gradually and monotonically down to a value that is even lower than that for pure Ti_2Ni . This is an indication of the occurrence of two opposing factors that contribute to the specific capacity. To elucidate this phenomenon, the chemical elemental characteristics of cobalt and nickel must be considered. As the atomic radius and atomic volume are greater for cobalt (1.47 Å and $6.7 \text{ cm}^3 \text{ mol}^{-1}$) than for nickel (1.42 Å and $6.59 \text{ cm}^3 \text{ mol}^{-1}$), the addition of cobalt with inevitably cause an expansion of the lattice cell and will thus enlarge the interstitial space and accordingly will benefit the hydrogen-storage process. On the other hand, as the atomic weight of cobalt (58.93) is also greater than that of nickel (58.67), the number of lattice cells per unit weight of alloy becomes less. This reduces the number of hydrogen-storage units and thus is detrimental to the hydrogen-storage process. Therefore, it is reasonable to assume that, with a cobalt addition of lower than a certain amount, the expansion of the lattice cells is dominant and will cause an increase in the specific capacity. At a critical content of cobalt, however, the expansion of any lattice cell will reach a saturation point that is caused by

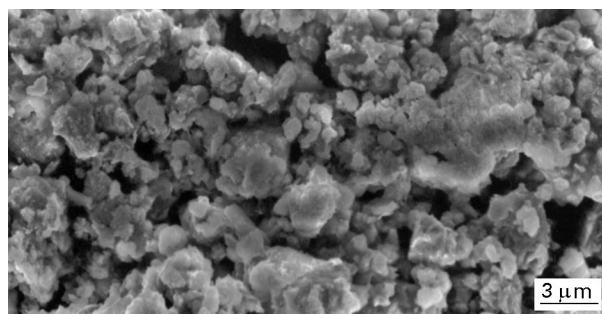


Figure 5 Scanning electron micrograph of Ti_2Ni alloy powder after 3 cycles.

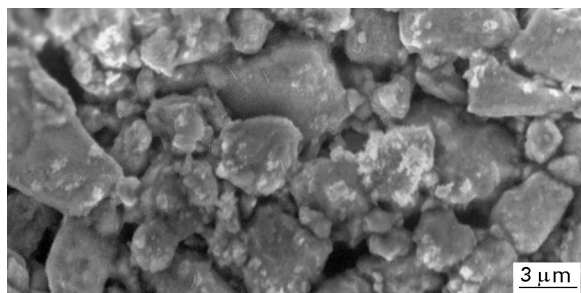


Figure 6 Scanning electron micrograph of $\text{Ti}_2\text{Ni}_{0.98}\text{Al}_{0.02}$ alloy powder after 8 cycles.

the restricting effect of the neighbouring expanded lattice cells. When this phenomenon begins to take place, the decrease in the number of lattice cells per unit weight of alloy with increasing cobalt content will become dominant and will give rise to a decrease in the specific capacity. Overall, the combined effect of the two opposite factors will inevitably result in an optimal value for the specific capacity. However, it is of note that the above explanation does not exclude other possibilities that give rise to the capacity loss of the electrode with higher cobalt addition. For example, with an increasing amount of cobalt addition, a new inactive phase might be formed which is not characterized by hydrogen storage but occupies some of the hydrogen storage elements, thus causing a decrease in the specific capacity of the electrode.

3.2. Potassium–boron addition

In order to increase the performance of Ti_2Ni hydrogen storage alloy electrode, K–B was added. The effects of K–B addition on the specific capacity and the cycle life of the electrode are discussed as follows.

The relation of the specific capacity and the specific capacity decay curves of the electrodes with different amount of K–B additions are shown in Figs 7 and 8, respectively. It can be seen that the specific capacity of the electrode increases with increasing K–B addition and the cycle life of the electrode is also greatly extended with K–B addition. To identify the individual effects of potassium and boron on the specific capacity and the cycle life of the electrode, additional amounts of boron were added to a precursor alloy with a minimum amount of potassium content, namely, $\text{Ti}_2\text{Ni}_{0.99}(\text{KB})_{0.01}$. The reason for utilizing

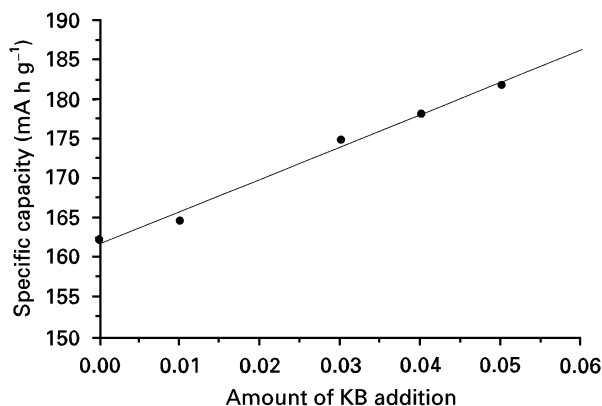


Figure 7 Variation in specific capacity of Ti_2Ni electrode with the amount of K-B addition.

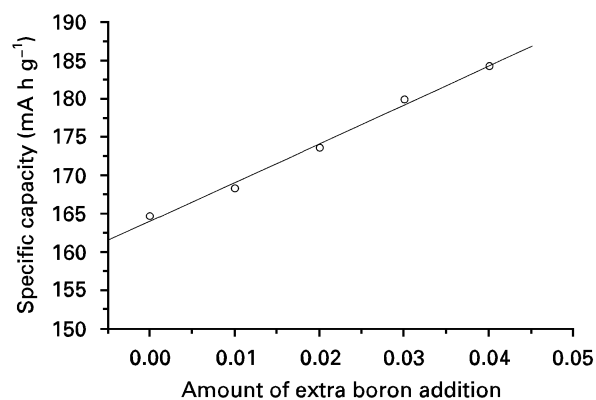


Figure 9 Variation in specific capacity of $\text{Ti}_2\text{Ni}_{0.99}(\text{KB})_{0.01}$ electrode with the different amounts of K-B addition.

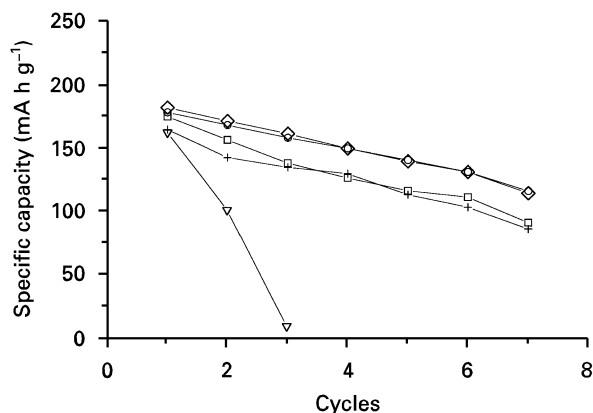


Figure 8 Specific capacity decay of the electrodes with different amounts of K-B addition. (◇), $\text{Ti}_2\text{Ni}_{0.95}(\text{KB})_{0.05}$; (○), $\text{Ti}_2\text{Ni}_{0.96}(\text{KB})_{0.04}$; (□), $\text{Ti}_2\text{Ni}_{0.97}(\text{KB})_{0.03}$; (+), $\text{Ti}_2\text{Ni}_{0.99}(\text{KB})_{0.01}$; (▽), Ti_2Ni .

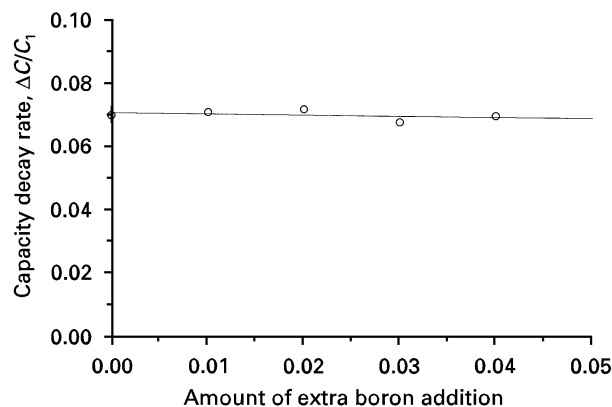


Figure 10 Effect of boron addition on the capacity decay rate of the electrodes.

potassium-added alloy as the precursor alloy is to take into account the elemental interactions of B and K. The specific capacity curve of the electrodes with various amounts of additional boron addition is given in Fig. 9. It can be clearly seen by comparing Figs 7 and 9 that the capacity variation in the electrode versus K-B content is in very good agreement with the capacity variation in the electrode versus additional B additions. Therefore it is reasonable to assume that boron, and not potassium, is responsible for the specific capacity increase of the electrodes with different amounts of K-B addition. The reason for this may be attributed to the fact that boron addition causes the formation of defects which act as the electrochemical active sites and thus increases the electrochemical activity of the alloy; this, in turn, increases the electrochemical discharge capacity of the electrode.

Similarly, to explore the reason responsible for the cycle life increase, the relation of the specific capacity decay rate of the electrode with different amounts of additional boron addition is shown in Fig. 10. It is of note from Fig. 10 that boron does not have any effect on the specific capacity decay rate of the electrode. Since the precursor alloy used was $\text{Ti}_2\text{Ni}_{0.99}(\text{KB})_{0.01}$, the interactions of K and B had already been taken into account; boron and K-B are excluded from being responsible for the cycle life increase of the Ti_2Ni

electrode. Therefore, it is reasonable to believe that the cycle life increase of the K-B-added Ti_2Ni electrode can be attributed to the effect of potassium addition to the alloy. The reason behind this may be as follows. It is well known that potassium is the activist element and so is easy to oxidize. Therefore it might be reasonable for us to assume that the potassium atoms present in the alloy act as a "micro-anode", and Ti_2Ni , the bulk hydrogen storage alloy, act as a "micro-cathode". From the theory of electrochemical cathodic protection we know that it is the "micro-anode" which is oxidized, i.e., sacrificed when a current is applied to the electrode while the "micro-cathode" is thus prevented from oxidation, i.e., protected. In the present study, potassium is sacrificed and the bulk Ti_2Ni hydrogen storage alloy is protected. Therefore the cycle life of the hydrogen-storage electrode can be greatly extended. However, this assumption may readily yield another problem. The sacrifice of potassium will inevitably give rise to a reduction in potassium content in the alloy after a certain number of cycles and therefore may lose its protection effect for further cycling. This may be explained as follows. Since the electrolyte used in the present work is 6 M KOH solution with a high K^+ ion concentration, therefore, although the potassium atoms present in the hydrogen-storage alloy dissolve and the potassium content may decrease initially, further dissolution of potassium atoms from the alloy is retarded owing to a decreasing chemical

potential of potassium atoms in the alloy and an increasing chemical potential of potassium ions in the electrolyte. Together with further dissolution of potassium, i.e. the decrease in the chemical potential of K atoms in the alloy and the increase in the chemical potential of K^+ ions in the electrolyte, there exists a time when the chemical potential of the potassium in the alloy equals the chemical potential of K^+ ions in the electrolyte. That is to say that equilibrium is reached. At this stage, the presence of potassium in the hydrogen-storage alloy may be maintained and its protection effect is thus maintained.

In summary, the effect of K–B addition to Ti_2Ni alloy can be described as follows. Potassium is responsible for the cycle life increase of the electrode while boron is responsible for the specific capacity increase.

3.3. Aluminium addition

The influences of aluminium addition on the specific capacity and cycle life of the electrode are shown in Figs 11 and 12, respectively. The specific capacity of $Ti_2Ni_{1-x}Al_x$ alloy electrodes severely decreases with increasing aluminium content (see Fig. 11), indicating that aluminium is detrimental to the specific capacity of the electrode. On the other hand, a much longer cycle life was observed for the alloy electrodes with aluminium additions than that of the electrode without any aluminium addition (pure Ti_2Ni alloy electrode), as is clearly shown in Fig. 12.

In order to find out the reasons responsible for the specific capacity decrease and the cycle life increase of the aluminium-added electrodes, “steady-state” potentiostatic polarization curves were obtained, as shown in Fig. 13. It is of note in Fig. 13 that active-to-passive transition was observed for the electrodes with aluminium contents of higher than 1 at % (0.03 in $Ti_2Ni_{0.97}Al_{0.03}$). However, the electrodes with a lower aluminium content did not show any obvious passivity, although their anodic current values are apparently much smaller than that of the pure Ti_2Ni alloy electrode. To explore the reason for the passivity of the electrodes, XRD was applied to analyse the alloy phase compositions, with the results shown in Figs 14a and b corresponding to Ti_2Ni and $Ti_2Ni_{0.97}Al_{0.03}$ alloys, respectively. $Ti_2Ni_{0.97}Al_{0.03}$ was given as an example of the aluminium-added alloys characterized by an active-to-passive transition. It can be found by comparison of Figs 14a and b that a new phase, Ti_2Al , was formed in $Ti_2Ni_{0.97}Al_{0.03}$ alloy preparation. Therefore it may be reasonable to ascribe the passivity to the new Ti_2Al phase. To verify this, Ti_2Al alloy was made in the same way as described above and was then confirmed by XRD analysis (see Fig. 14c). Consequently, the “steady-state” potentiostatic polarization curve of Ti_2Al electrode was obtained, as shown in Fig. 15. It is evident in Fig. 15 that Ti_2Al alloy exhibits a definite active-to-passive transition performance. Therefore it is reasonable to conclude that the Ti_2Al phase coexists with $Ti_2Ni_{1-x}Al_x$ alloy and is actually responsible for the passivity of the aluminium-added electrodes.

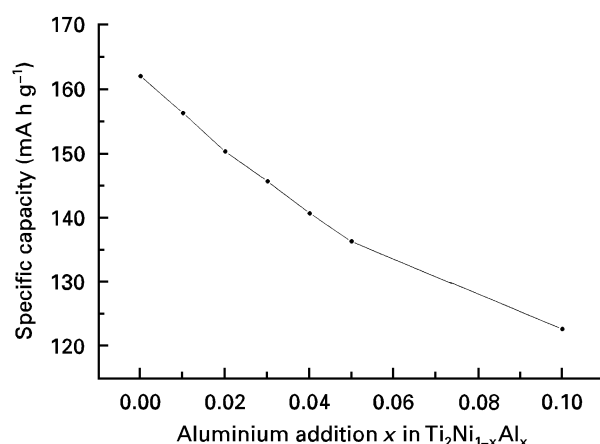


Figure 11 Dependence of specific capacity on the amounts of aluminium addition.

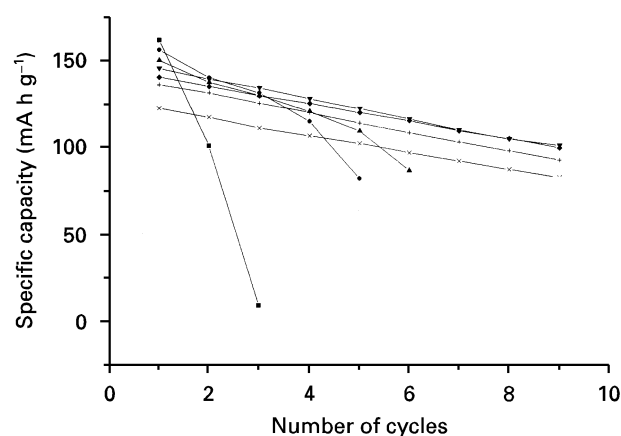


Figure 12 Specific capacity decay of the electrodes with different amounts of aluminium addition versus number of cycles. (■), Ti_2Ni ; (●), $Ti_2Ni_{0.99}Al_{0.01}$; (▲), $Ti_2Ni_{0.98}Al_{0.02}$; (▼), $Ti_2Ni_{0.97}Al_{0.03}$; (◆), $Ti_2Ni_{0.96}Al_{0.04}$; (+), $Ti_2Ni_{0.95}Al_{0.05}$; (×), $Ti_2Ni_{0.90}Al_{0.10}$.

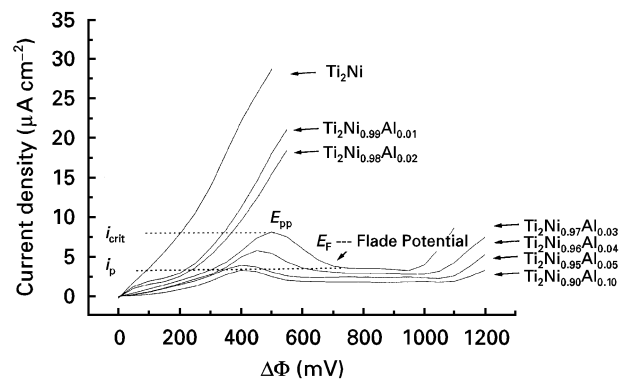


Figure 13 “Steady-state” potentiostatic polarization curves of the electrodes with different amounts of aluminium additions in 6 M KOH aqueous solution (Hg/HgO reference electrode).

From the discussion above, the cycle life increase and the specific capacity decrease of the electrode with aluminium additions may be explained as follows. As was mentioned above, the specific capacity of the electrode decreases as aluminium addition increases. This may be attributed to the following two reasons.

1. The aluminium added inevitably captures some of the titanium atoms and leads to the formation of

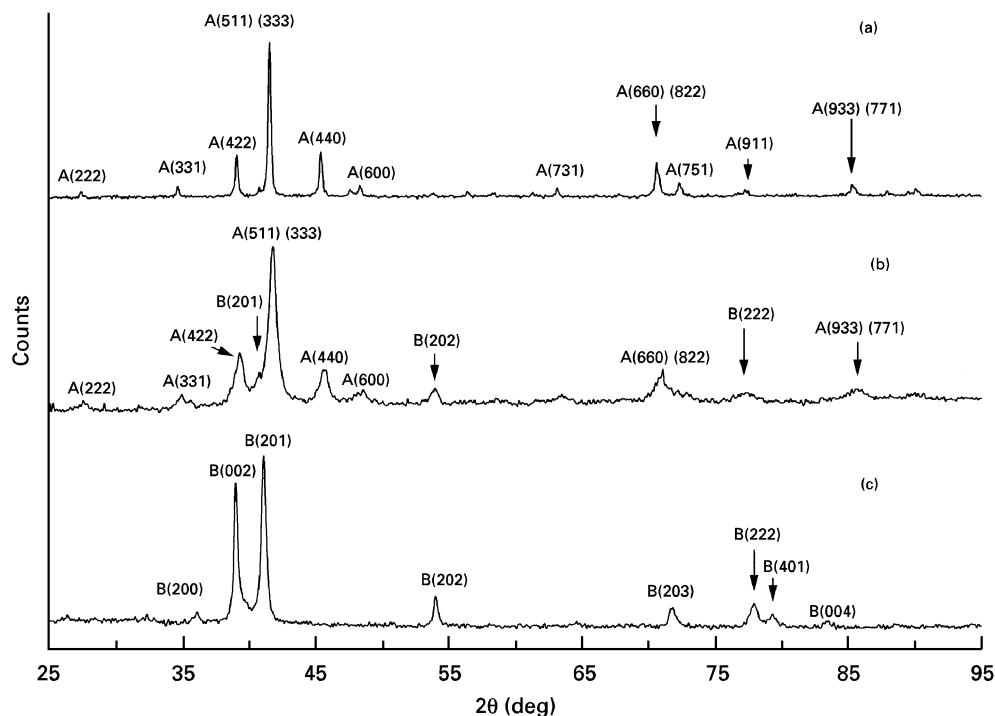


Figure 14 XRD analyses of alloy compositions of (a) Ti_2Ni alloy, (b) $\text{Ti}_2\text{Ni}_{0.97}\text{Al}_{0.03}$ alloy and (c) Ti_2Al alloy. A, Ti_2Ni ; B, Ti_2Al .

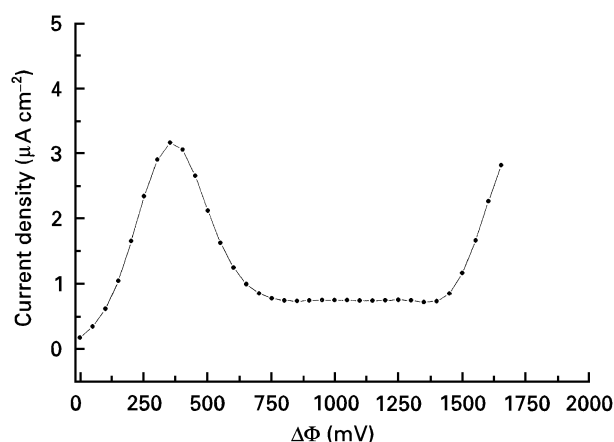


Figure 15 "Steady-state" potentiostatic polarization curve of Ti_2Al alloy electrode in 6 M KOH aqueous solution (Hg/HgO reference electrode).

a new Ti_2Al phase which is not capable of storing hydrogen, resulting in a decrease in the capacity per unit weight of alloy.

2. During the discharge process, metal hydride decomposes and the atomic hydrogen generated diffuses out to the surface of the electrode. Since the passivation layer formed inhibits the diffusion of atomic hydrogen from within the alloy powder and therefore slows down the electrode kinetics, the discharge efficiency of the electrode is thus decreased and the specific capacity of the electrode is thus decreased.

For the two reasons above, the addition of aluminium is detrimental to the performance of the electrode and is therefore to be minimized from the viewpoint of the specific capacity of the electrode.

On the other hand, aluminium addition was observed to be beneficial to the cycle life of the electrode. This may be explained as follows. When electrodes fabricated from the alloys with an aluminium content higher than 1 at % ($\text{Ti}_2\text{Ni}_{0.97}\text{Al}_{0.03}$) were exposed to an electrolyte of 6 M KOH during the discharge process, nucleation and growth of the passivation layer commenced and developed. Because the hydrogen-storage alloy was shielded by a dense passivation layer, it could no longer be attracted directly by the agents (electrolyte); therefore the oxidation of the alloy may be reduced and the cycle life of the electrode is thus increased. Within the aluminium content range of 0.33 at % (0.01 in $\text{Ti}_2\text{Ni}_{0.99}\text{Al}_{0.01}$) to 0.67 at % (0.02 in $\text{Ti}_2\text{Ni}_{0.98}\text{Al}_{0.02}$), the formation of the Ti_2Al phase was not detected by XRD analysis and the anodic polarization curves did not show significant active-to-passive transition. Nevertheless, it is still evident in Fig. 13 that the anodic current of the electrodes fabricated from $\text{Ti}_2\text{Ni}_{0.99}\text{Al}_{0.01}$ and $\text{Ti}_2\text{Ni}_{0.98}\text{Al}_{0.02}$ is much smaller than that of the electrode fabricated from pure Ti_2Ni alloy. This may be suggestive of the fact that the Ti_2Al phase was actually also formed in the alloys with a low aluminium content. The reason that it is not detectable by XRD analysis may be attributed to its very low content. Therefore the effectiveness in increasing the corrosion resistance of the electrode still exists, as is shown in Fig. 13. As for the pure Ti_2Ni electrode, the cycle life is rather short because the electrode is kept in an active state and in direct contact with the strongly oxidizing electrolyte during the entire discharge process.

From all the results and discussion above, the effects of elemental substitutions (Co, K-B and Al) on the performance of the Ti_2Ni hydrogen-storage alloy electrode can be briefly summarized as follows.

Cobalt and boron are beneficial while aluminium is detrimental to the specific capacity of the electrode. Cobalt, potassium and aluminium are all beneficial to the cycle life of the electrode, although by different mechanisms. Boron was found not to contribute to the cycle life of the electrode while potassium did not contribute to the specific capacity of the electrode.

4. Conclusions

1. Cobalt was found to be beneficial not only to the specific capacity but also to the cycle life of the electrode. The optimal value of cobalt addition is recommended from our work to be about 0.67 wt % ($\text{Ti}_2\text{Ni}_{0.98}\text{Co}_{0.02}$).

2. Potassium is very effective in increasing the cycle life of the electrode while boron is beneficial to the specific capacity of the electrode. The recommended amount of K-B addition to Ti_2Ni is 1.33 wt % ($\text{Ti}_2\text{Ni}_{0.96}(\text{KB})_{0.04}$) from our work.

3. Aluminium was shown to be responsible for the passivity of the $\text{Ti}_2\text{Ni}_{1-x}\text{Al}_x$ electrode by means of the

formation of a new phase, Ti_2Al , thus significantly increasing the cycle life of the electrode. On the debit side, however, it is detrimental to the specific capacity of the electrode. Therefore on indefinite increase in aluminium is definitely not advantageous. It is recommended from our work that the amount of aluminium addition be 1 wt % ($\text{Ti}_2\text{Ni}_{0.97}\text{Al}_{0.03}$).

References

1. B. LUAN, N. CUI, H. K. LIU, H. ZHAO and S. X. DOU, *J. Power Sources* **52** (1994) 295.
2. *Idem.*, *ibid.* **55** (1995) 101.
3. *Idem.*, *J. Alloys Compounds* **233** (1996) 225.
4. *Idem.*, *J. Power Sources* **55** (1995) 197.
5. *Idem.*, *Int. J. Hydrogen Energy* **21** (5) (1996) 373.
6. S. VENKATESAN, M. FETCENKO, B. REICHMAN and K. C. HONG, in "Proceedings of the 24th Intersociety Energy Conversion Engineering Conference", Washington, DC, 6-11 August 1989, Vol. 3 (1989) 1659.

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