Effect of cobalt addition on the performance of titanium-based hydrogen-storage electrodes

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Abstract

The influence of cobalt addition on the performance of a Ti_2Ni hydrogen-storage alloy is examined. The cobalt addition is confirmed by energy dispersive spectroscopy compositional analysis. X-ray diffraction (XRD) results reveal that cobalt partially substitutes the nickel in the Ti_2Ni alloy. Charge/discharge cycle measurements show that the specific capacity of Ti_2Ni electrodes increases with cobalt addition, reaches a maximum at a cobalt content of 0.67 at.% ($Ti_2Ni_{0.98}Co_{0.02}$), and then falls with further addition. The cycle life of Ti_2Ni electrodes increases significantly with cobalt addition. Scanning electron microscopy analysis reveals that cobalt is effective in reducing the disintegration of the Ti_2Ni hydrogen-storage alloy powder, while XRD analysis shows that cobalt restricts the oxidation of the Ti_2Ni hydrogen-storage alloy. By contrast, the addition of cobalt does not inhibit the formation of the irreversible $Ti_2NiH_{0.5}$ hydride phase.

Keywords: Cobalt; Electrodes; Hydrogen-storage electrodes; Titanium; Nickel

1. Introduction

Titanium-based alloys are promising for certain hydrogen-storage applications due to the combination of a high volume density of hydrogen and the relatively high thermodynamic stability of titanium hydride [1–13]. Despite this, there are very few reports of titanium-based alloys being used as electrodes for rechargeable batteries [13–16]. Previous work by the authors [15,16] revealed that the cycle life of electrodes fabricated from Ti_2Ni electrode is rather short. There are three reasons for the rapid capacity loss, namely: (i) oxidation of the alloy powder; (ii) formation of the irreversible $Ti_2NiH_{0.5}$ hydride phase, and (iii) disintegration of the alloy powder. A room-temperature, surface microencapsulation technique was applied [15] and found to be effective in reducing the alloy oxidation. To increase further the charge/discharge cycle life of Ti_2Ni hydrogen-storage electrodes, the authors attempted to modify the alloy composition by adding certain elements to the Ti_2Ni alloy. Different amounts of cobalt were added to form tertiary alloys of different compositions because of the following reasons: (i) the similar electron configurations of cobalt ($(3d)^7(4s)^2$) and nickel ($(3d)^8(4s)^2$); (ii) the close, but slightly greater, atomic radius of cobalt (1.47 Å) compared with nickel (1.42 Å), and

(iii) the close, but slightly greater, atomic volume of cobalt (6.7 cm^3/mol) compared with nickel (6.59 cm^3/mol). It was expected that the addition of cobalt would inhibit the lattice expansion and contraction during hydriding and dehydriding (i.e., during the charging and the discharging processes) and would thus reduce alloy powder disintegration and, consequently, increase the cycle life of the electrode. Since it was predicted in the previous work [16] that inhibition of the irreversible formation and accumulation of the $Ti_2NiH_{0.5}$ hydride phase may lead to an increase in capacity and a decrease in the rate of capacity loss, this hydride phase has been examined in the studies reported here.

2. Experimental

2.1. Electrode preparation

Alloys of nominal composition Ti_2Ni, $Ti_2Ni_{0.98}Co_{0.02}$, $Ti_2Ni_{0.95}Co_{0.05}$, $Ti_2Ni_{0.8}Co_{0.2}$ and $Ti_2Ni_{0.6}Co_{0.4}$ were prepared by arc-melting and chill casting in a copper hearth under argon protection and with repeated melting and turning to ensure homogeneity. Care was taken to ensure that all the minor alloy constituents were melted within the ingots. The alloy ingots were crushed and ground
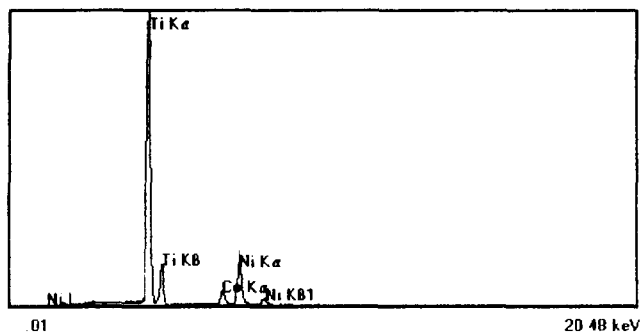
Fig. 1. Energy dispersive spectrum of nominal $Ti_2Ni_{0.98}Co_{0.02}$ alloy.

to powders of below 100 mesh using a Fritsch Planetary Mill (Pulverisisette 5). The powder was mixed with 10 wt.%. polyvinyl alcohol (PVA) solution at a ratio of approximately 10:1. Each mixed powder was pasted on to a foam-nickel sheet of 2 cm×2 cm×0.2 cm. The pasted foam-nickel sheets were dried and pressed at a pressure of 55 kN/cm² to form hydrogen-storage electrodes.

2.2. Charge/discharge procedure

Charge/discharge cycles were applied by using an in-house automatic charge/discharge unit. All electrodes were charged to gassing voltage and then, after a rest period of 30 min, were deeply discharged galvanostatically at a current density of 20 mA/g down to 0.70 V (versus Hg/HgO reference electrode). The discharged

electrodes were then charged again after a rest period of 30 min.

2.3. Morphology, composition and phase analysis

The crystalline structure and lattice parameters were obtained by using an X-ray diffractometer (XRD) (Philips PW 1010). Cobalt addition was confirmed by energy dispersive spectroscopy (EDS) analysis (Link System EDS Detector with Moran Software). Microstructural examination was performed with scanning electron microscopy (SEM) (Leica/Cambride Stereoscan 440).

3. Results and discussion

Qualitative EDS analysis confirmed the presence of cobalt in the tertiary alloys as expected. The spectrum for the nominal $Ti_2Ni_{0.98}Co_{0.02}$ alloy is shown in Fig. 1. XRD diffraction analysis of uncycled electrodes fabricated from the alloys with different amounts of cobalt revealed that the diffraction patterns are the same as that of the pure Ti_2Ni alloy. The diffraction pattern of $Ti_2Ni_{0.98}Co_{0.02}$ electrode (Fig. 2) is given as an example of cobalt-added electrodes and can be compared with the diffraction pattern of pure Ti_2Ni electrode shown in Fig. 3. It can be seen that cobalt addition does not change the lattice parameters of the Ti_2Ni alloy. This indicates that cobalt atoms exist at some of the positions originally occupied by nickel
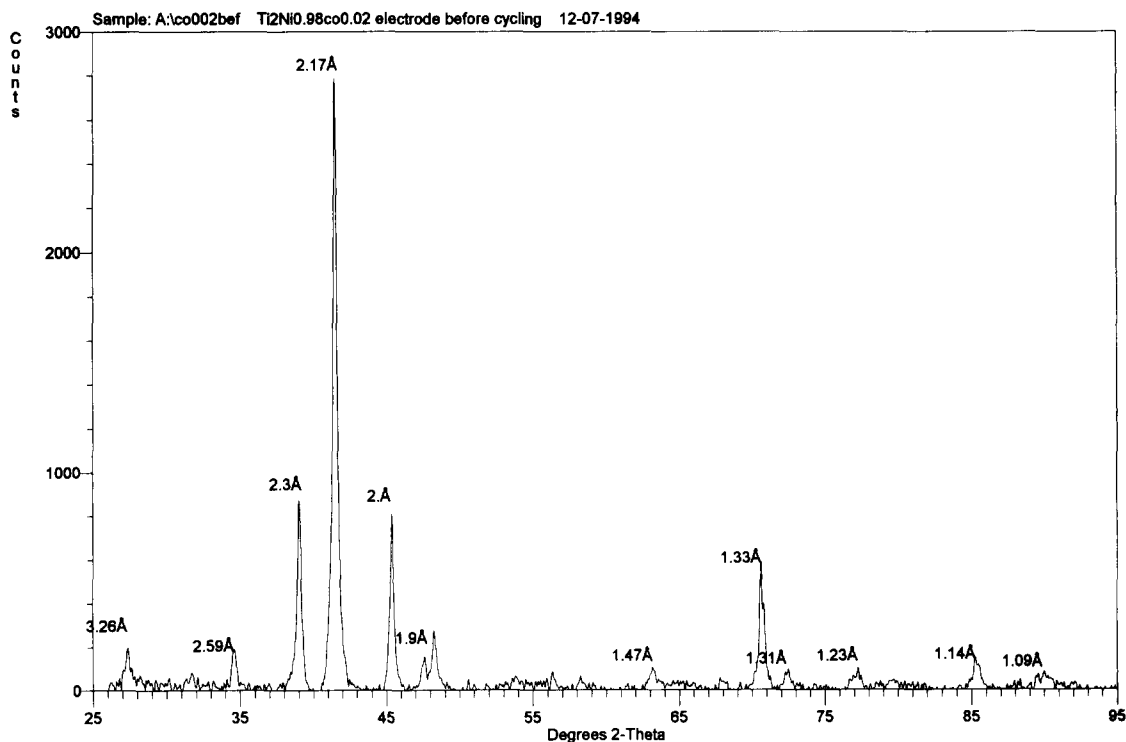

Fig. 2. X-ray diffraction pattern of $Ti_2Ni_{0.98}Co_{0.02}$ electrode before cycling.
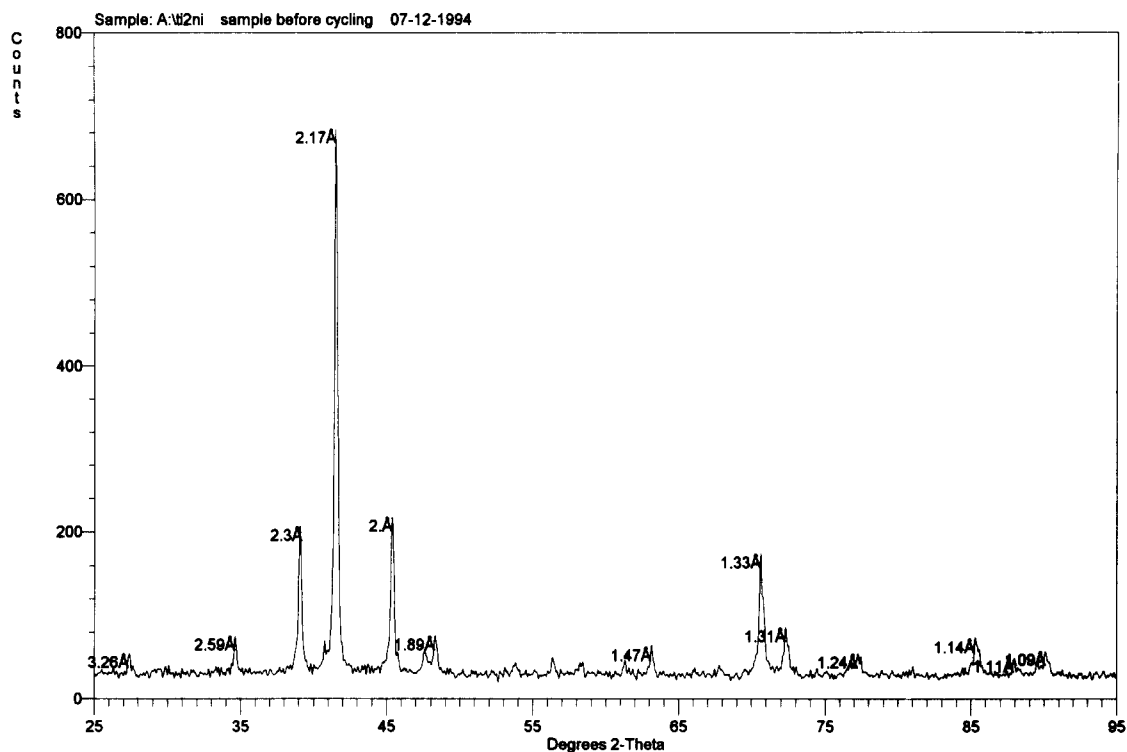
Fig. 3. X-ray diffraction pattern of Ti_2Ni electrode before cycling.

Table 1
Percentage of capacity retention by electrodes with different cobalt contents at different cycles

Electrode	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6
Ti_2Ni	1.00	0.62	0.06			
$Ti_2Ni_{0.98}Co_{0.02}$	1.00	0.85	0.77	0.65	0.60	0.52
$Ti_2Ni_{0.95}Co_{0.05}$	1.00	0.72	0.64	0.54	0.48	0.42
$Ti_2Ni_{0.8}Co_{0.2}$	1.00	0.62	0.37	0.26	0.20	0.16
$Ti_2Ni_{0.6}Co_{0.4}$	1.00	0.55	0.27	0.16	0.13	0.05

atoms in the lattice structure. In another words, the action of cobalt is to substitute partially the nickel atoms in the lattice cells of Ti_2Ni alloy. Therefore, the basic lattice structure of Ni_2Ni alloy is retained and the hydrogen-storage characteristic of the alloy is thus maintained. XRD analysis was also performed on cobalt-added electrodes after cycling. The results for $Ti_2Ni_{0.98}Co_{0.02}$ are given in Fig. 4. The previous investigation [16] revealed that formation and accumulation of the irreversible $Ti_2NiH_{0.5}$ phase is the predominant cause of the premature capacity loss of Ti_2Ni electrodes. From Fig. 4, it can seen that two phases coexist, namely: $Ti_2(NiCo)H_{0.5}$ and Ti_2Ni. The existence of the $Ti_2(NiCo)H_{0.5}$ phase indicates that the incorporation of cobalt in Ti_2Ni is not effective in preventing, or inhibiting, the formation and accumulation of the $Ti_2NiH_{0.5}$ phase.

The discharge curves for electrodes with different amounts of cobalt are presented in Figs. 5 to 9. The results show that the $Ti_2Ni_{0.98}Co_{0.02}$ electrode has the

best discharge performance. An additional comparison of electrode performance is given in Fig. 10 in terms of capacity–decay curves. To demonstrate further the effect of cobalt addition on the capacity decay of Ti_2Ni electrodes, the percentage of capacity retention of the electrodes at various cycles is given in Table 1, while the relationship between the specific capacity during the first three cycles and the corresponding cobalt content is illustrated in Fig. 11. The data in Table 1 and Fig. 11 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. For example, the percentage of capacity retention of a $Ti_2Ni_{0.98}Co_{0.02}$ electrode after three cycles is 77% while that of the Ti_2Ni electrode is only about 6%. This clearly indicates that cobalt is very effective in lengthening the cycle life of the Ti_2Ni electrodes. The reason for this may be due to the fact that cobalt addition enlarges the lattice cell and hence reduces the lattice expansion and contraction during the corresponding
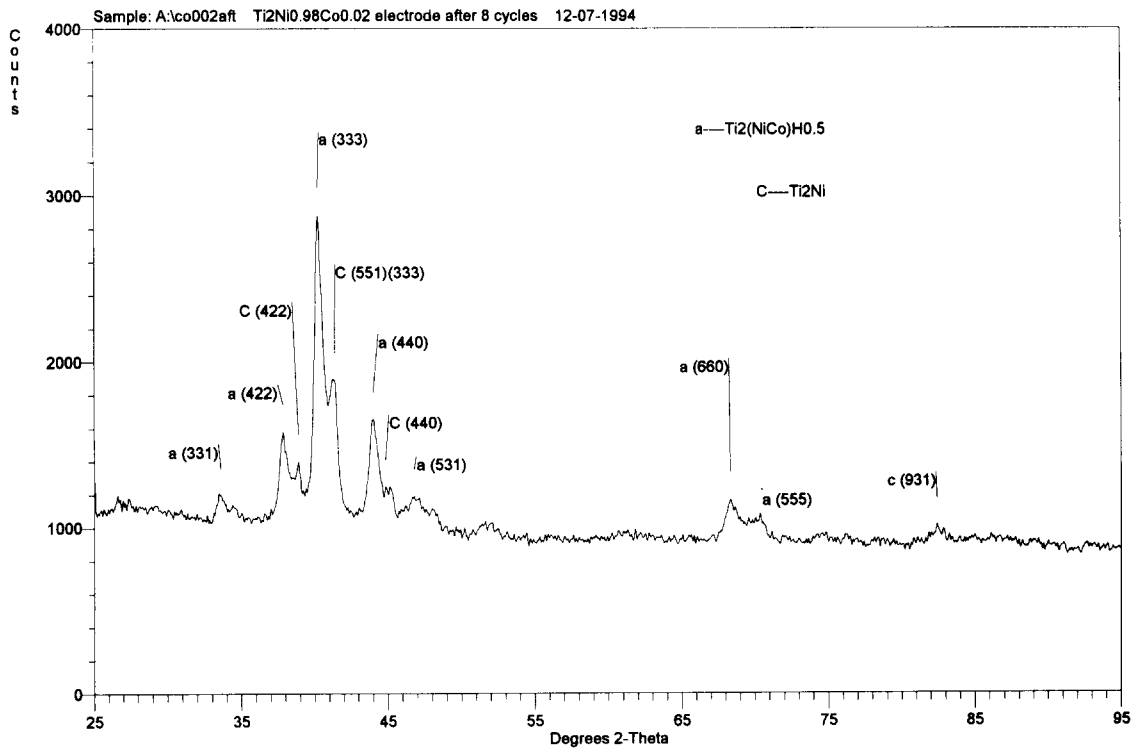
Fig. 4. X-ray diffraction pattern of $Ti_2Ni_{0.98}Co_{0.02}$ electrode after eight cycles.
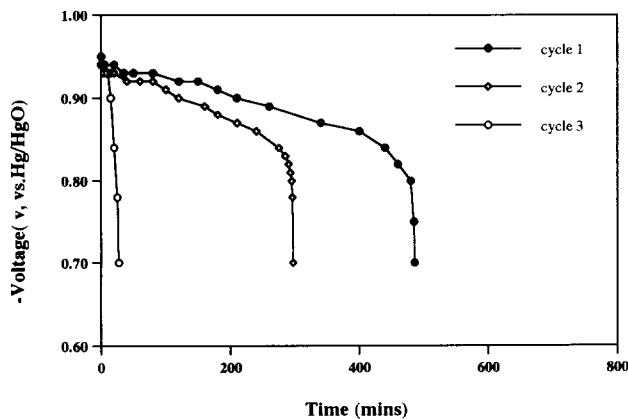

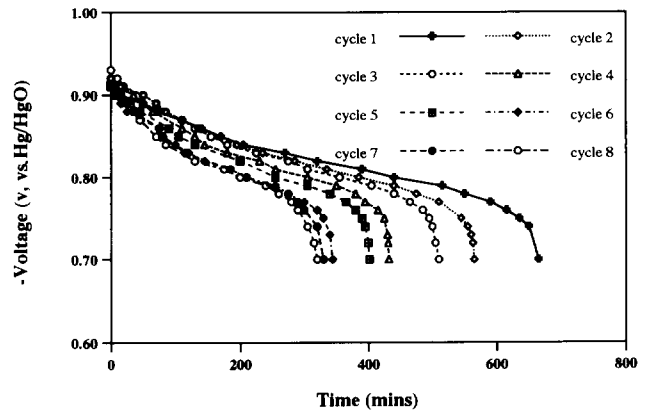Fig. 5. Galvanostatic discharge curves for Ti_2Ni electrode at a current density of 20 mA/g in 6 M KOH.

Fig. 6. Galvanostatic discharge curves for a $Ti_2Ni_{0.98}Co_{0.02}$ electrode at a current density of 20 mA/g in 6 M KOH.

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 on reducing the rate of powder disintegration, as shown in Figs. 12 and 13. It can be seen that the alloy without cobalt addition has disintegrated severely after only three cycles (Fig. 12), whereas the alloy powder with a cobalt content of 0.67 at.% is only slightly degraded, even up to eight deep cycles (Fig. 13).

Among the electrodes with different cobalt additions, the $Ti_2Ni_{0.98}Co_{0.02}$ electrodes has the most significant effect (Figs. 10 and 11). The variation in electrode specific capacity at different numbers of cycles versus

cobalt content is displayed in Fig. 11. With only 0.67 at.% (i.e., 0.02 in $Ti_2Ni_{0.98}Co_{0.02}$) cobalt, the specific capacity of Ti_2Ni is largely increased. However, with further increase of cobalt up to 13.33 at.% (i.e., 0.4 in $Ti_2Ni_{0.6}Co_{0.4}$), the specific capacity decreases gradually and monotonously down to a value that is even lower than that for pure Ti_2Ni. This is an indication of the concurrence 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 cm³/mol) than for nickel (1.42 Å and 6.59 cm³/mol), addition of cobalt will inevitably cause an
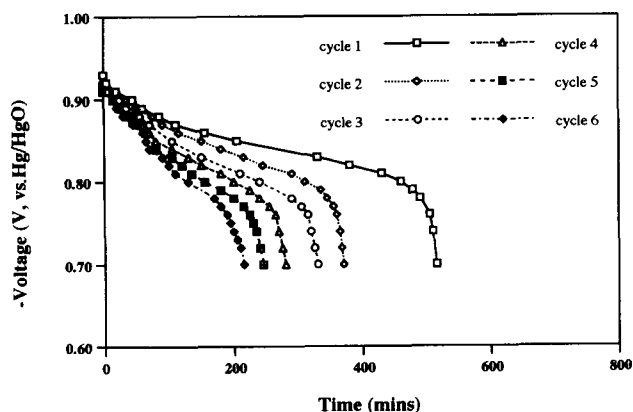
Fig. 7. Galvanostatic discharge curves for a $Ti_2Ni_{0.95}Co_{0.05}$ electrode at a current density of 20 mA/g in 6 M KOH.
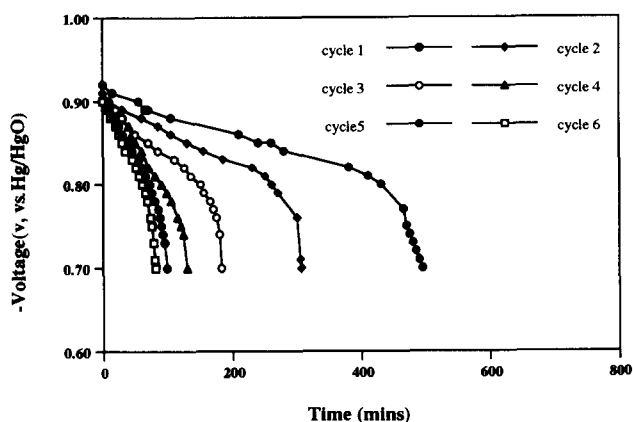

Fig. 8. Galvanostatic discharge curves for a $Ti_2Ni_{0.8}Co_{0.2}$ electrode at a current density of 20 mA/g in 6 M KOH.
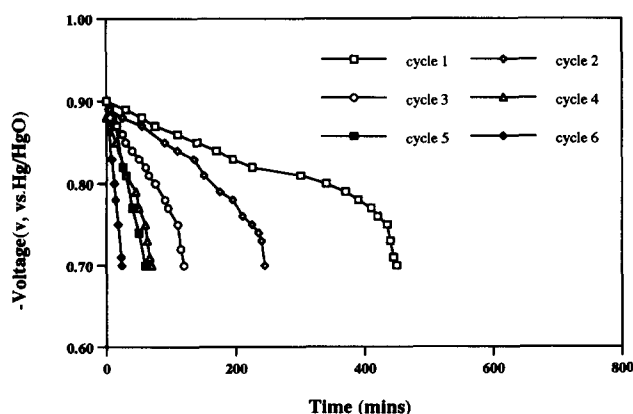

Fig. 9. Galvanostatic discharge curves for a $Ti_2Ni_{0.6}Co_{0.4}$ electrode at a current density of 20 mA/g in 6 M KOH.
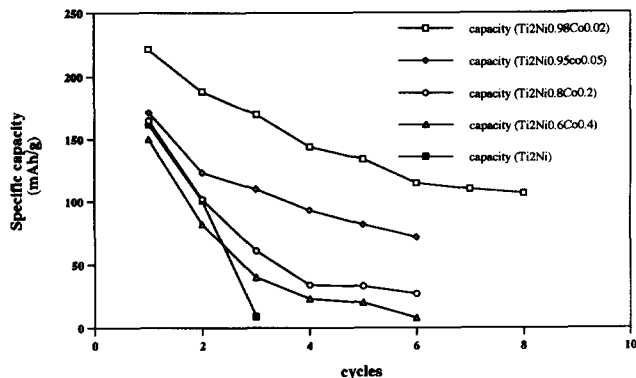

Fig. 10. Comparison of capacity decay curves for electrodes with different cobalt contents.
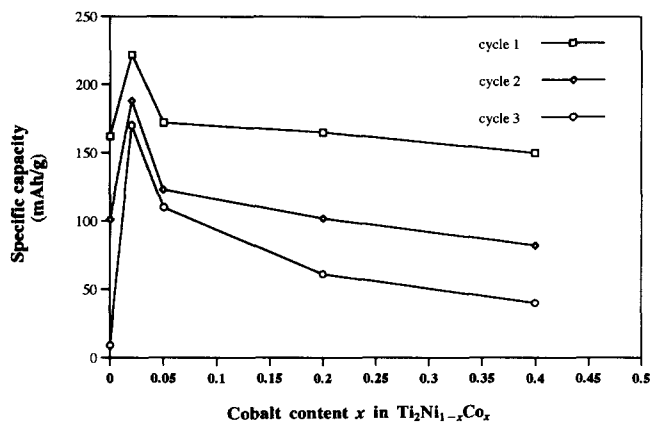

Fig. 11. Variation of specific capacity of electrodes with different cobalt contents during first three cycles.

Fig. 12. Electron micrograph of Ti_2Ni alloy powder after three cycles.

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 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
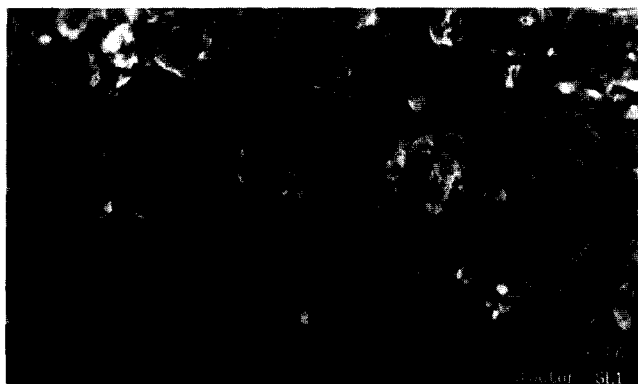
Fig. 13. Electron micrograph of $Ti_2Ni_{0.98}Co_{0.02}$ alloy powder after eight cycles.

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. Considering the above assumptions and discussion together with the experimental results, the results presented in Fig. 11 may be explained as follows. Within a cobalt content range of 0 to 0.67 at.%, lattice expansion of the alloy is predominant and the specific capacity of the alloy increases with increasing cobalt content. Nevertheless, when the cobalt content is between 0.67 and 13.33 at.%, a decrease in the lattice cell number per unit weight of alloy becomes dominant and the specific capacity of the alloy decreases monotonously. Therefore, an optimal value of specific capacity is obtained from a $Ti_2Ni_{0.98}Co_{0.02}$ electrode (i.e., 0.67 at.% cobalt).

4. Conclusions

Based on the above discussion, the effect of cobalt addition on the performance of Ti_2Ni hydrogen-storage electrodes may be summarised as follows.
1. XRD analysis provides the following results:
• The added cobalt substitutes partially the nickel atoms in the Ti_2Ni lattice structure and this enables the alloy to maintain its hydrogen-storage characteristics
• cobalt is effective in reducing the disintegration of Ti_2Ni alloy powder during charge/discharge processes; this is confirmed by SEM studies of electrode morphology
• cobalt has no effect on the formation and accumulation of $Ti_2(NiCo)H_{0.5}$; the existence of the latter phase is confirmed by XRD analysis.
2. Charge/discharge results show that a $Ti_2Ni_{0.98}Co_{0.02}$ electrode has the highest specific capacity, as well as the highest capacity-retention rate. This is possibly due to the concurrence of two opposing factors that contribute to the specific capacity variation, namely: enlargement of the lattice cells and reduction of lattice cell number per unit weight. With a cobalt content

below 0.67 at.%, enlargement of the lattice cells is dominant and thus benefits the hydrogen-storage process. By contrast, with a cobalt content greater than 0.67 at.%, reduction of lattice cell number becomes dominant and this is detrimental to the hydrogen-storage process. Therefore, the highest specific capacity of the electrode occurs at a cobalt content of 0.67 at.% (i.e., for a $Ti_2Ni_{0.98}Co_{0.02}$ electrode).

Previous work [16] revealed that oxidation of the Ti_2Ni alloy is one of the causes of capacity decay of the electrode. In the present study, however, XRD phase analysis of the $Ti_2Ni_{0.98}Co_{0.02}$ electrode after eight cycles did not reveal the existence of any oxidant (Fig. 4). Therefore, it is concluded that cobalt addition is also effective in increasing the oxidation resistance of Ti_2Ni hydrogen-storage alloys during charge/discharge cycles. Nevertheless, the mechanism of such action has still to be elucidated.

In summary, from the above experimental results and discussion, it may be concluded that cobalt addition is effective in lengthening the cycle life of Ti_2Ni hydrogen-storage electrodes by means of reducing the disintegration and increasing the oxidation resistance of the alloy powder. However, cobalt additions of up to 0.67 at.% also improve the specific capacity of the electrodes; the $Ti_2Ni_{0.98}Co_{0.02}$ electrode exhibits the highest specific capacity. Nevertheless, cobalt is not effective in either preventing or inhibiting the formation and accumulation of the irreversible $Ti_2NiH_{0.5}$ hydride phase. To increase further the capacity and the cycle life of Ti_2Ni hydrogen-storage electrodes, additions of other elements will be investigated.

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