

Short Communication

Mechanism of early capacity loss of Ti_2Ni hydrogen-storage alloy electrode

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Abstract

The mechanism underlying the rapid, early, capacity loss of titanium-based (Ti_2Ni) hydrogen-storage alloys is examined via X-ray diffraction analysis. The formation and accumulation of $\text{Ti}_2\text{NiH}_{0.5}$, a hydride phase that cannot be reversibly charged/discharged according to the experimental results, is proposed as a dominant cause of the early capacity loss of such electrodes.

Keywords: Electrodes; Hydrogen-storage alloy; Titanium; Nickel

1. Introduction

Oxidation and disintegration are believed to be prominent factors that are associated with the capacity loss of hydrogen-storage alloys when subjected to charge/discharge cycles [1–4]. An interesting phenomenon reported previously [5] is the overlap in the first two cycles of the discharge curves of electrodes that are fabricated from uncoated Ti_2Ni alloy powder and Ti_2Ni powder coated at room temperature and at 80 °C (Fig. 1). This indicates the presence of a further contributing factor to the capacity loss that occurs during the early charge/discharge cycles of Ti_2Ni hydrogen-storage alloys. As is well known, four hydride phases of Ti_2Ni alloys exist, namely: $\text{Ti}_2\text{NiH}_{0.5}$, Ti_2NiH , Ti_2NiH_2 , and $\text{Ti}_2\text{NiH}_{2.5}$. The $\text{Ti}_2\text{NiH}_{2.5}$ alloy has the highest hydrogen-storage capacity while the $\text{Ti}_2\text{NiH}_{0.5}$ alloy has the lowest. Furthermore, the $\text{Ti}_2\text{NiH}_{0.5}$ hydride phase was found in the spent Ti_2Ni electrode in the previous work [5]. Consequently, the formation and accumulation of $\text{Ti}_2\text{NiH}_{0.5}$ during the charge/discharge process may be another factor that is linked directly with capacity loss, as was hitherto assumed to be the case [5]. To confirm this, an X-ray diffraction (XRD) technique was used to analyse systematically the phases that are formed at each stage during the first two charge/discharge cycles.

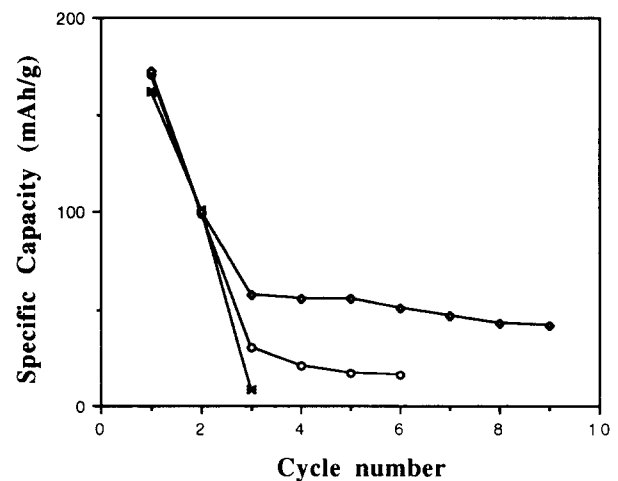


Fig. 1. Capacity decay curves of (x) uncoated Ti_2Ni electrode, (o) high temperature powder-coated Ti_2Ni electrode, and (diamond) room temperature powder-coated Ti_2Ni electrode.

2. Experimental

Ti_2Ni alloy was made using an arc furnace under argon protection. All materials used were provided by the Aldrich Chemical Company Inc. The ingot obtained was crushed and ground into a powder of below 100 mesh. One gram of the powder was mixed with a poly(vinyl alcohol) solution at the ratio of 10:1 and was then casted on to a foam nickel sheet of 2.0 cm ×



Fig. 2. Experimental procedure.

2.0 cm × 0.2 cm. The sheet, when dry, was then pressed at a pressure of 15 kN/cm² to form a hydrogen-storage electrode. The electrode was now ready for charge/discharge cycling and XRD analysis.

The electrode was both charged (to gassing voltage) and deep-discharged (to -0.20 V versus Hg/HgO reference electrode) galvanostatically at a current density of 20 mA/cm² in a 6 M KOH. At each stage of being charged and discharged, the electrode was analysed by XRD and performed on a Philips PW 1010 diffractometer. The procedure was then repeated to obtain XRD analysis for a second charge/discharge cycle.

The overall experimental procedure is illustrated briefly in Fig. 2.

3. Results and discussion

XRD patterns are shown in Fig. 3 through Fig. 6. The corresponding XRD data are summarized in Table 1 through Table 5. The results are summarized as follows:

(i) The original electrode fabricated from the hydrogen-storage alloy is composed of Ti₂Ni, as indicated in previous work [5]; see Fig. 3.

(ii) After the first charge, there is clear evidence of the development of two phases, Ti₂NiH and Ti₂NiH_{0.5}; see Fig. 4.

(iii) Ti₂NiH_{0.5} and Ti₂Ni co-exist after the first discharge; see Fig. 5.

(iv) Three phases, i.e., Ti₂NiH_{0.5}, Ti₂NiH and Ti₂Ni, co-exist after the second charge; see Fig. 6.

(v) Ti₂NiH_{0.5} exists together with a new phase, (Ti₂Ni)₂O, after the second discharge; see Fig. 7.

In summary, the findings show that two titanium nickel hydride phases exist when Ti₂Ni is charged, namely, Ti₂NiH_{0.5} and Ti₂NiH. After being discharged (see Fig. 5), Ti₂NiH is transformed reversibly into Ti₂Ni but the Ti₂NiH_{0.5} hydride phase still remains. This indicates that Ti₂NiH_{0.5} cannot be charged and discharged reversibly and, therefore, does not contribute to the discharge capacity of the electrode. It would appear that the part of the Ti₂Ni hydrogen-storage alloy that forms the Ti₂NiH_{0.5} phase loses its reversible charge/discharge performance.

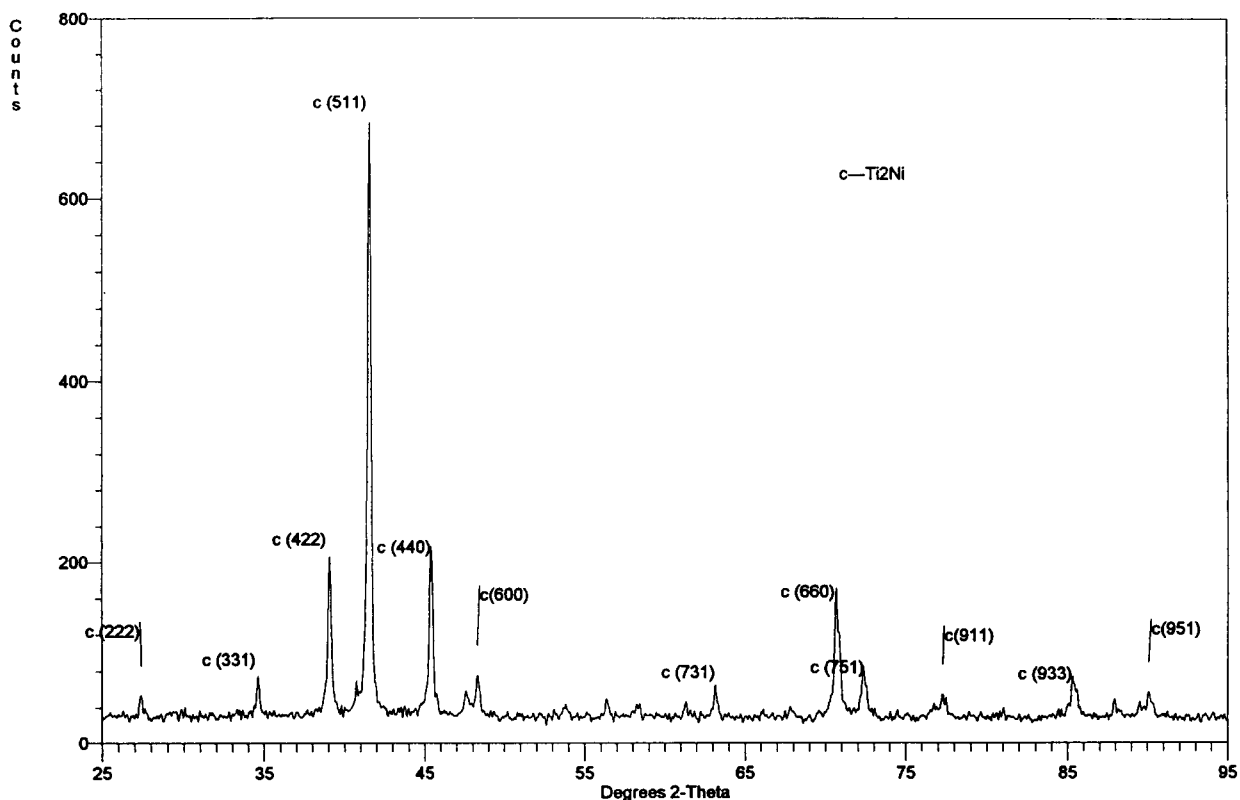


Fig. 3. X-ray diffraction pattern for Ti₂Ni electrode before charge/discharge cycling.

Table 1
X-ray diffraction data for Ti_2Ni electrode before cycling (corresponding to Fig. 3)

	Ti_2Ni											
<i>d</i> -Space (measured)	3.26	2.59	2.30	2.17	2.00	1.89	1.47	1.33	1.31	1.24	1.14	1.09
<i>d</i> -Space (ASTM standard)	3.26	2.59	2.30	2.17	1.99	1.88	1.47	1.33	1.30	1.24	1.13	1.09
(<i>hkl</i>)	222	331	422	511	440	600	731	660	751	911	933	951

Table 2
X-ray diffraction data for $Ti_2NiH_{0.5}$ and Ti_2NiH electrodes after the first charge (corresponding to Fig. 4)

	$Ti_2NiH_{0.5}$					Ti_2NiH					
<i>d</i> -Space (measured)	2.34	2.21	2.03	1.35	1.12	2.71	2.40	2.26	2.08	1.95	1.37
<i>d</i> -Space (ASTM standard)	2.34	2.21	2.03	1.35	1.13	2.71	2.41	2.27	2.07	1.96	1.37
(<i>hkl</i>)	422	333	440	660	862	331	422	333	440	600	555

Table 3
X-ray diffraction data for Ti_2Ni and $Ti_2NiH_{0.5}$ electrodes after the first discharge (corresponding to Fig. 5)

	Ti_2Ni						$Ti_2NiH_{0.5}$					
<i>d</i> -Space (measured)	3.26	2.59	2.30	2.17	2.04	1.91	1.47	2.35	2.22	2.04	1.33	1.13
<i>d</i> -Space (ASTM standard)	3.26	2.59	2.30	2.17	2.03	1.91	1.47	2.34	2.21	2.03	1.33	1.13
(<i>hkl</i>)	222	331	422	511	440	600	731	422	333	440	555	862

Table 4
X-ray diffraction data for $Ti_2NiH_{0.5}$, Ti_2NiH and Ti_2Ni electrodes after the second charge (corresponding to Fig. 6)

	$Ti_2NiH_{0.5}$						Ti_2NiH			Ti_2Ni				
<i>d</i> -Space (measured)	2.34	2.22	2.03	1.91	1.66	1.33	1.13	2.28	2.07	1.24	2.31	2.18	2.00	1.91
<i>d</i> -Space (ASTM standard)	2.34	2.21	2.04	1.91	1.66	1.33	1.13	2.27	2.07	1.24	2.30	2.17	1.99	1.91
(<i>hkl</i>)	422	333	440	600	444	555	862	333	440	931	422	511	440	531

Table 5
X-ray diffraction data for $Ti_2NiH_{0.5}$ and $(Ti_2Ni)_2O$ electrodes after the second discharge (corresponding to Fig. 7)

	$Ti_2NiH_{0.5}$						$(Ti_2Ni)_2O$					
<i>d</i> -Space (measured)	2.63	2.33	2.22	2.03	1.91	1.33	2.31	2.18	2.00	1.41	1.39	1.34
<i>d</i> -Space (ASTM standard)	2.63	2.34	2.21	2.03	1.91	1.33	2.31	2.18	2.00	1.41	1.38	1.34
(<i>hkl</i>)	331	422	333	440	600	555	422	333	440	800	733	660

When the electrode undergoes a second charge, the $Ti_2NiH_{0.5}$ phase is still present. It is reasonable that an additional amount of $Ti_2NiH_{0.5}$ hydride phase is formed from Ti_2Ni , as can be qualitatively shown by comparing Fig. 6 with Fig. 4. This reaction during the second charging process thus gives rise to an accu-

mulation of the $Ti_2NiH_{0.5}$ hydride phase. The Ti_2NiH phase is again formed from the hydriding of Ti_2Ni during the second charging process. This time, however, some Ti_2Ni remains and may be attributed to the now partly disintegrated Ti_2Ni powder losing its hydrogen-storage ability and thus becoming incapable of being

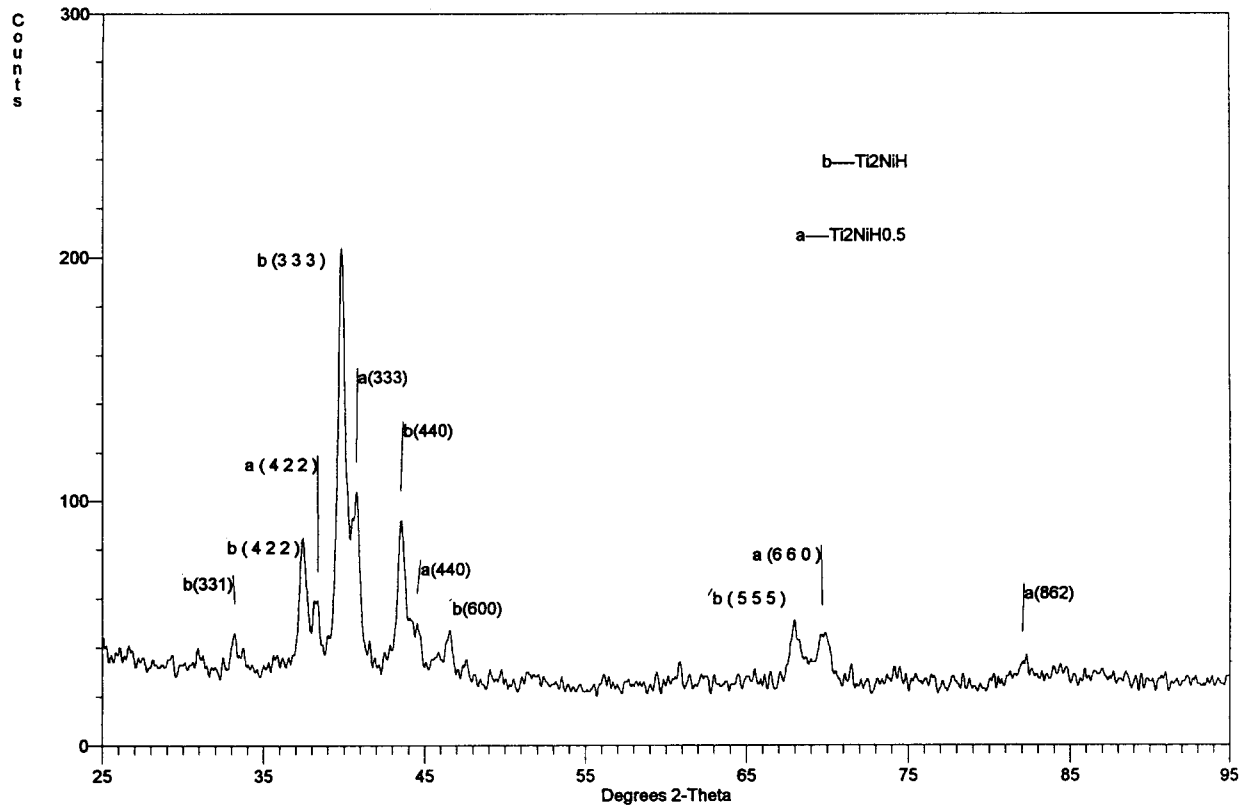


Fig. 4. X-ray diffraction pattern for Ti_2Ni electrodes after first charge.

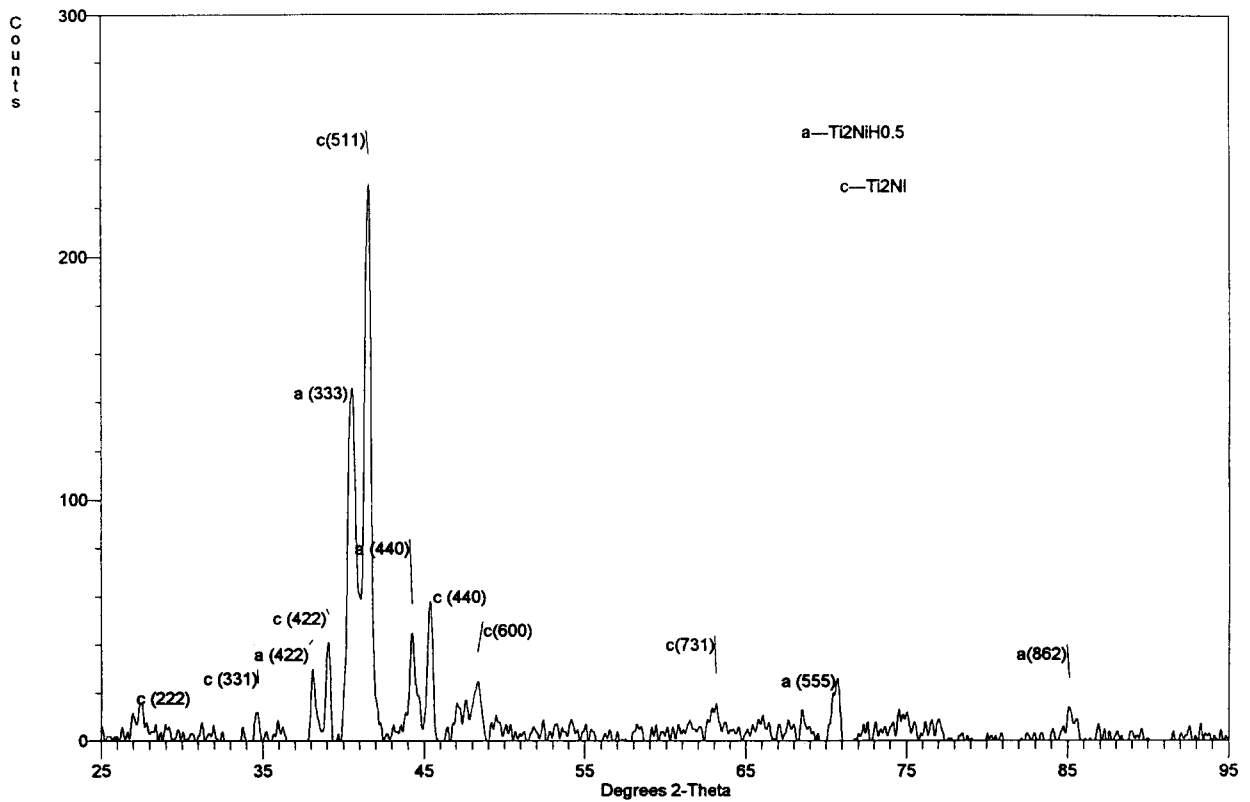


Fig. 5. X-ray diffraction pattern for Ti_2Ni electrodes after first discharge.

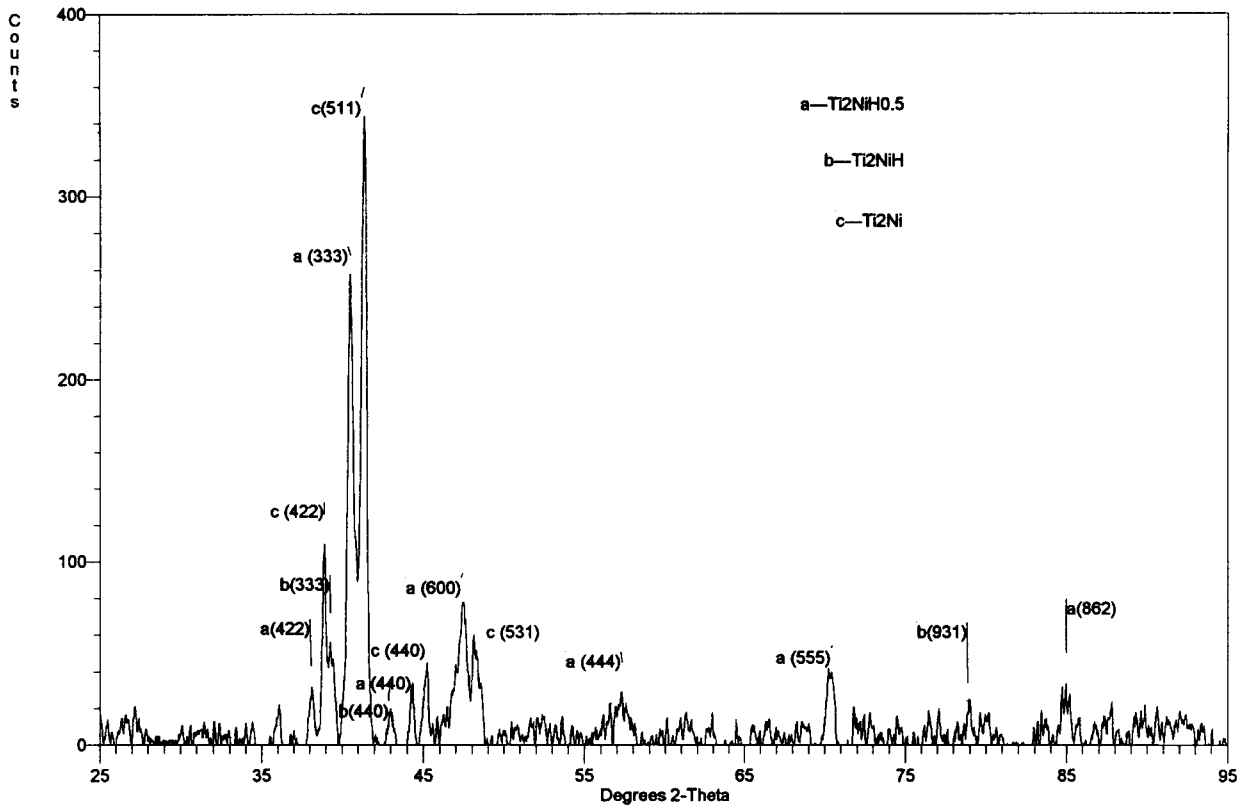


Fig. 6. X-ray diffraction pattern for Ti₂Ni electrodes after second charge.

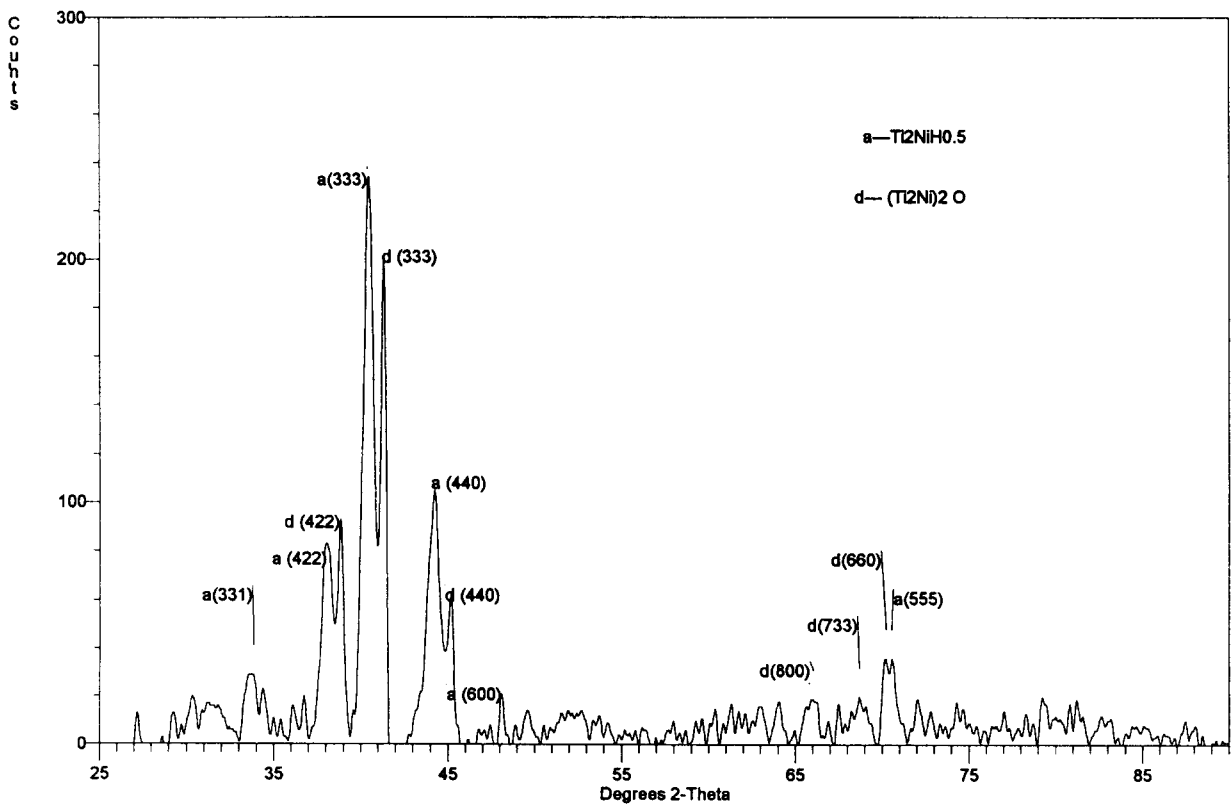


Fig. 7. X-ray diffraction pattern for Ti₂Ni electrodes after second discharge.

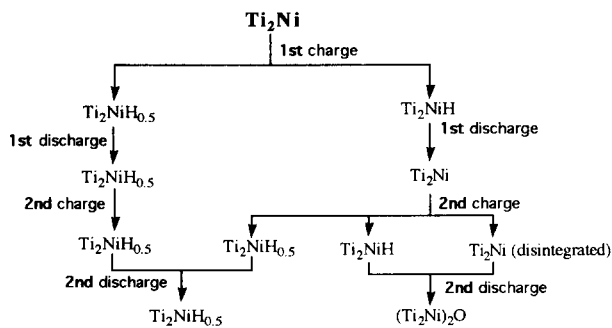


Fig. 8. Schematic of capacity decay in Ti_2Ni hydrogen-storage alloys.

hydrided during the second charging process [5]. After the second discharge (see Fig. 7), it can be seen that the $\text{Ti}_2\text{NiH}_{0.5}$ phase is still present and that the Ti_2Ni (both disintegrated and dehydrided from Ti_2NiH) has been oxidized to become $(\text{Ti}_2\text{Ni})_2\text{O}$. This is consistent with the capacity of the third discharge (see Fig. 4) which drops to an almost negligible level.

The results and discussions above clearly indicate that the produced $\text{Ti}_2\text{NiH}_{0.5}$ hydride phase cannot be reversibly charged and discharged and, thus, will accumulate inside the hydrogen-storage alloy to cause significant capacity loss during the early charge/discharge cycles. The capacity decay process of Ti_2Ni hydrogen-storage alloys is illustrated schematically in Fig. 8.

The mechanism outlined above facilitates the explanation of the capacity decay curves of the electrodes fabricated from uncoated Ti_2Ni alloy powder and Ti_2Ni alloy powder coated at high temperature (80°C) and at room temperature (see Fig. 1). In the first two cycles, the formation and accumulation of the $\text{Ti}_2\text{NiH}_{0.5}$ hydride phase determines the capacity loss. This is because the process is irreversible and thus makes no contribution to the discharge capacity of the Ti_2Ni hydrogen-storage alloy. Furthermore, the formation and accumulation of the $\text{Ti}_2\text{NiH}_{0.5}$ hydride phase is internal and, therefore, is independent of surface micro-encapsulations. Accordingly, the three curves overlap each other during the first two cycles, as shown in Fig. 1. After this period, formation of the $\text{Ti}_2\text{NiH}_{0.5}$ hydride phase is possibly saturated and oxidation of the Ti_2Ni phase dominates the capacity decay process, to form $(\text{Ti}_2\text{Ni})_2\text{O}$ on the powder surface. Because micro-encapsulation greatly increases the oxidation resistance of the alloy powder, the micro-encapsulated alloy maintains its capacity to a greater degree than the uncoated alloy, as

indicated in Fig. 1. The fact that the capacity decay of the low-temperature micro-encapsulated alloy is significantly slower than that of the high-temperature counterpart might be due to the former alloy having a more condensed coating with lower porosity and, consequently, better protection against oxidation [5].

The $\text{Ti}_2\text{NiH}_{0.5}$ hydride phase occupies some of the Ti_2Ni powder, but makes no contribution towards the discharge capacity of the alloy. To increase the capacity and retard the capacity loss of Ti_2Ni hydrogen-storage alloys, further research aimed at eliminating or reducing the formation and accumulation of the $\text{Ti}_2\text{NiH}_{0.5}$ hydride phase during charge cycles is required.

4. Conclusions

1. The formation of $\text{Ti}_2\text{NiH}_{0.5}$ hydride phase is observed inside Ti_2Ni hydrogen-storage alloys during early cycles. Once formed, the compound cannot be reversibly charged and discharged. Therefore, it provides no contribution to the discharge capacity of Ti_2Ni electrodes.

2. $\text{Ti}_2\text{NiH}_{0.5}$ formation and accumulation dominates the capacity loss during early cycles, while oxidation and disintegration of the Ti_2Ni powder become the determining factors during later cycles.

3. In order to increase the capacity and retard the capacity loss of Ti_2Ni hydrogen-storage alloys, the formation and accumulation of $\text{Ti}_2\text{NiH}_{0.5}$ hydride during charge cycles must be restricted or prevented.

Acknowledgements

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