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The analysis of the two discharge plateaus for Ti–Ni-based metal hydride electrode alloys

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Abstract

In some conditions, the multi-phase composition of the hydrogen storage electrode alloy can be reflected on its discharge curve. In this paper, the discharge curves of the Ti–Ni-based hydrogen storage alloys have be analyzed using electrochemical techniques and XRD. We concluded that the appearance of the two discharge plateaus on the discharge curves of the $Ti_{0.5}Al_{0.25}Ni_{0.25}$ alloy and $Ti_3Ni_{1.7}M_{0.3}$ (M = Ni, Al, Co, Cr) alloys is related to their multi-phase composition and multi-phase hydride formation. The appearance of the first fastigiated plateau is the result of together releasing hydrogen of TiNi and Ti_2Ni phases. The secondary flat plateau represents releasing hydrogen process of only the Ti_2Ni phase.

Keywords: Hydrogen storage alloy; Multi-phase composition; Ti–Ni-based alloy; Discharge curve; XRD

1. Introduction

The nickel-metal hydride rechargeable battery exhibits excellent performances, such as energy density on a volume and weight and cycle life. The metal hydride alloys included rare-earth-based AB_5-type with $CaCu_5$-type structure [1,2], AB_2-type Laves phase [3], V–Ti-based solid solution [4] and Mg-based alloys [5], etc. We found that the two discharge plateaus appear at the discharge curves at 353 K for Ti_3Ni_2-type alloy electrode [6]. The relationship between the high-rate dischargeability and the diffusion coefficient and exchange current for $Ti_{0.5}Al_{0.25}Ni_{0.25}$ alloy electrodes was reported [7]. The previous researches show that the appearance of the two discharge plateaus is related to the multi-phase composition of the alloys. In this paper, the two discharge plateaus at 353 K for Ti_3Ni_2 alloy electrode are investigated in detail, and the analysis of the discharge curves of the $Ti_{0.5}Al_{0.25}Ni_{0.25}$ alloy and $Ti_3Ni_{1.7}M_{0.3}$ (M = Al, Co, Cr) have been done. The author hope that the research is helpful to theoretical research and development of new type hydrogen storage alloys.

2. Experimental

The alloys were prepared by induction melting in a water-cooled boat under argon atmosphere and re-melted four times to ensure homogeneity. The alloy ingot was decrepitated into small particles by hydriding and dehydriding cycles for both XRD analysis and electrochemical tests. The alloy powder was mixed with Ni powder in the weight ratio of 1:2, and pressed to form a round-disc electrode of 10 mm diameter (about 100 mg hydrogen storage alloy per pellet). Electrodes were tested at 353 K in an open cell in an electrolyte of 6 mol/l KOH solution with Hg/HgO/6 mol/l KOH as the reference electrode and $Ni(OH)_2$/NiOOH as the counter electrode.

For XRD analysis, a Philips X'pert MPD diffractometer with Cu Kα radiation (0.15405 nm) was used with 40 kV ×30 mA, the scanning rate was 0.02°/s, the step time was 0.5 s.

3. Results

3.1. The characteristics of the discharge curves of the Ti_3Ni_2 electrode

The discharge curves of the Ti_3Ni_2 alloy electrode at 353 K were given in Fig. 1. The discharge current density is

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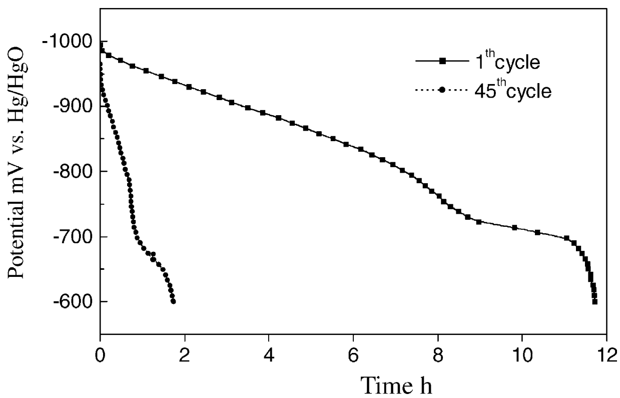

Fig. 1. The discharge curves of Ti_3Ni_2 at 353 K at 25 mA/g.

25 mA/g. The two discharge plateaus can be seen from this curve: one being the fastigiate plateau at −980 to −790 mV regions, and another being the flatter at −740 to −690 mV region. After 45 cycles, the discharge plateaus' potentials became more positive, from which we believe that as-cast Ti_3Ni_2 alloy consists of two different phases at least. When the temperature is lower than 323 K, there is only one plateau on the discharge curves. This type of potential profile with hydrogen concentration indicates that there is two phase in mother alloy at least.

3.2. The X-ray analysis

The ingot of the Ti_3Ni_2 alloy was difficult to be crushed because of its roughness. The XRD pattern of the as-cast Ti_3Ni_2 alloy was given in Fig. 2A. The Fig. 2B is the XRD pattern of the Ti_3Ni_2 alloy that was put under 60 atm hydrogen pressure for 24 h. Fig. 2C is the one of Ti_3Ni_2 alloy was put under 60 atm hydrogen gas for 120 h and the Fig. 2D is the pattern of this alloy that was cycled 90 numbers in 6 M KOH solutions. Analyzed, it can be found that the main phases of the as-cast alloy are a cubic TiNi phase with CsCl structure and a cubic Ti_2Ni phase. After charging hydrogen 120 h at 60 atm hydrogen pressure, the block alloy was crushed into powders. The XRD analysis shows that the main phases of the hydrided alloy prepared by hydrogen decrepitating are a cubic $Ti_2NiH_{0.5}$ phase and a cubic TiNiH phase. For the cycled in KOH solution samples, a cubic Ti_2NiH phase with a Fe_3W_3C-type structure and a cubic TiNiH phase could be found. The presence of two hydrides is consistent with the appearance of two discharge plateaus.

3.3. The analysis on the reaction processes corresponding to the two discharge plateaus

When the electrode of the Ti_3Ni_2 alloy is discharging in KOH solution, what electrochemical reaction processes are the processes, which correspond to the two discharge plateaus in discharge curves?

After 24 h charging hydrogen at 60 atm hydrogen pressure, the block alloy cannot be crushed into powders. The X-ray analysis of the block Ti_3Ni_2 alloy proved that the main phase is TiNi and $Ti_2NiH_{0.5}$ phase, as shown in Fig. 2B. In other words, the hydrogen was stored in Ti_2Ni phase. This

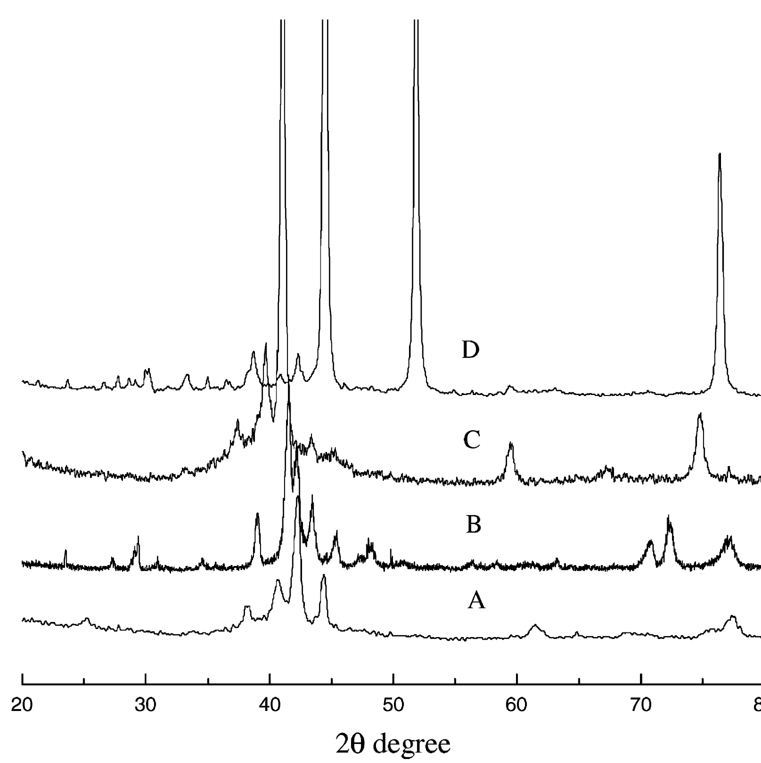

Fig. 2. The X-ray diffraction patterns of Ti_3Ni_2 alloy: (A) as-cast; (B) 60 atm Hydrogen, 24 h; (C) 60 atm, 120 h; (D) after 90 cycles in 6 M KOH.

result indirectly proved that the hydride of Ti_2Ni phase is more stable than that of TiNi phase.

Since Justi et al. [8] reported the application of Ti–Ni alloy as hydrogen storage electrode materials, in the past decades many works on the electrode properties of the Ti–Ni–H systems have been done by many researchers [9–12]. For the hydride of TiNi phase, a majority of the hydrogen was electrochemically dischargeable in KOH solution, but for the hydride of Ti_2Ni phase only 40–50% of the hydrogen was reversible. From the point of the view of the reaction thermodynamics, the hydride of Ti_2Ni phase should be more stable than that of TiNi phase because the content of the Ti-element, which has a strong trend to combine with hydrogen, in Ti_2Ni is more than in TiNi.

Based the above-mentioned discussions and the experiment results, we believe the discharge process is following: at the initial stage of discharge, the TiNi phase firstly releases the stored hydrogen, at the same time, the part of hydrogen stored in Ti_2Ni phase has a possibility to take part in discharge process. Because more than two phase had taken part in the discharge process, therefore, the first plateau at its discharge curve (as shown in Fig. 1) is very fastigiated. As the discharge process continued, the electrode potential changed to positive direction. When the potential became more positive about −750 to −700 mV (versus Hg/HgO), almost all hydrogen for TiNi phase was released, but the Ti_2Ni phase still keeping on releasing the hydrogen. In this temporality, the TiNi is electro-catalytic to promote the releasing hydrogen in Ti_2Ni. The secondary discharge plateau represents only the releasing-hydrogen process of Ti_2Ni phase, therefore, it is very flat, as shown in Fig. 1.

3.4. The discharge curves of $Ti_3Ni_{1.7}M_{0.3}$ (M = Cr, Co, Al) and $Ti_{0.5}Al_{0.25}Ni_{0.25}$ alloy electrodes

The discharge curves of $Ti_3Ni_{1.7}M_{0.3}$ (M = Cr, Co, Al) and $Ti_{0.5}Al_{0.25}Ni_{0.25}$ alloy electrodes were shown in Fig. 3. It can be seen clearly from Fig. 3 that the two discharge plateaus appear at the discharge curves. The XRD patterns

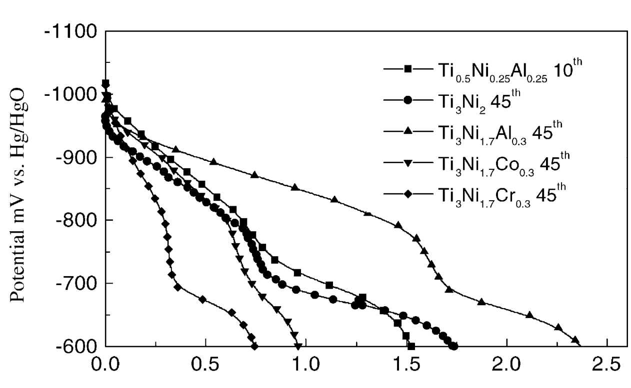

Fig. 3. The discharge curves of $Ti_3Ni_{1.7}M_{0.3}$ (M = Cr, Co, Al) and $Ti_{0.5}Al_{0.25}Ni_{0.25}$ alloys at 353 K.

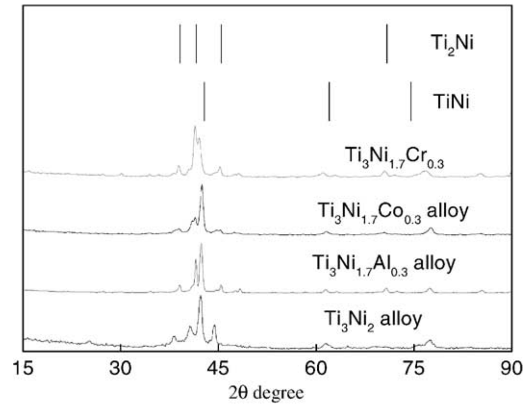

Fig. 4. The XRD patterns of the $Ti_3Ni_{1.7}M_{0.3}$ (M = Ni, Cr, Co, Al) alloys.

of the $Ti_3Ni_{1.7}M_{0.3}$ (M = Cr, Co, Al) alloys were given in Fig. 4 and the XRD pattern of $Ti_{0.5}Ni_{0.25}Al_{0.25}$ alloy was given in Fig. 5. After the alloying element, such as Cr, Co or Al substituting a part of Ni in Ti_3Ni_2 alloy, the main phases have not changed, as shown in Fig. 4. The $Ti_{0.5}Ni_{0.25}Al_{0.25}$ alloy is composite of four phases: the cubic TiNi phase with CsCl type structure, the cubic Ti_2Ni phase, the hexagonal Ti_2Al phase and square $Ti_8(TiAl_{23})$ phase.

We believe that the appearance of the two discharge plateaus for the $Ti_3Ni_{1.7}M_{0.3}$ (M = Cr, Co, Al) and $Ti_{0.5}Al_{0.25}Ni_{0.25}$ alloy electrodes were related to their multi-phase composition. The appearance of the first fastigiated plateau is a result of releasing hydrogen of TiNi and Ti_2Ni phase and the appearance of the secondary flat plateau was related to the releasing hydrogen of the Ti_2Ni phase.

From theoretical viewpoint, the number of the discharge plateau in the electrochemical discharge curve of metal hydride in alkaline solution is consistent with that in pressure–composition isotherm curve that is measured in equilibrium or quasi-equilibrium condition in hydrogen gas atmosphere. But in practical, the number of the discharge plateau in electrochemical curves is always smaller than that in *P–C–T* curves. First, the relationship of the

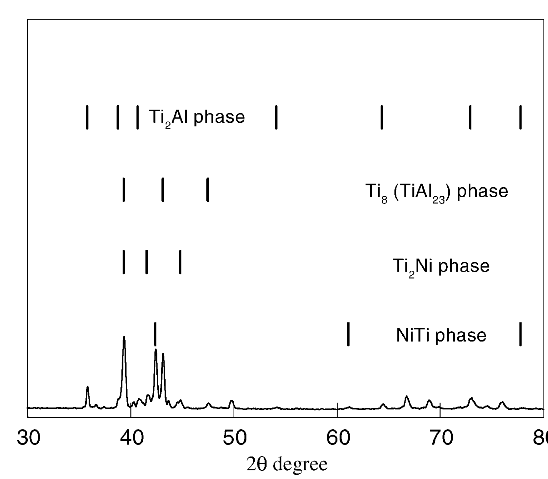

Fig. 5. The XRD pattern of the as-cast $Ti_{0.5}Ni_{0.25}Al_{0.25}$.

electrochemical potential ϕ with the equilibrium hydrogen gas pressure P is expressed as follows:

$$\phi = A + B \log P_{H_2}$$

where A and B represent a constant, P_{H_2} represents the equilibrium hydrogen gas pressure in P–C–T curve. The logarithmic function conversion from hydrogen gas pressure to electrode potential lowers the plateau pressure difference in P–C–T curve. Secondary, if an equilibrium plateau pressure is larger than 5 atm or smaller than 0.001 atm, then the corresponding discharge plateau would not appear because its corresponding electrode potential is larger than that at which water decomposes into hydrogen gas and oxygen gas or smaller than −0.6 V (versus Hg/HgO) that is the cutoff voltage of discharge of metal hydride electrode.

The existence of the second discharge plateau is related to the second phase. The sudden increase of the discharge capacity with the temperature can be explained by the existence of the second phase. With cycling, the width of each plateau becomes smaller and the total discharge capacity decreases. The main reason is the corrosion, i.e. the decrease of the relative content of the effective phase being storing hydrogen.

4. Conclusion

For the $Ti_3Ni_{1.7}M_{0.3}$ (M = Ni, Co, Al or Cr) and $Ti_{0.5}Al_{0.25}Ni_{0.25}$ hydrogen storage electrode alloys, the two discharge plateaus appeared at their discharge curves when the temperature is 353 K. The appearance of the two discharge plateaus on their discharge curves is due to their multi-phase composition: the main phase for the $Ti_3Ni_{1.7}M_{0.3}$ (M = Ni, Co, Al or Cr) alloys is a cubic TiNi and cubic Ti_2Ni phase; the $Ti_{0.5}Al_{0.25}Ni_{0.25}$ alloy is composite of four phases, i.e. TiNi, Ti_2Ni, Ti_2Al and $Ti_8(TiAl_{23})$ phases. The first fastigiated plateau (about −980 to −790 mV versus Hg/HgO) represents releasing hydrogen process of both TiNi and Ti_2Ni phase and the secondary flat one corresponded to releasing hydrogen process of the Ti_2Ni phase.

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