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Crystal structure and some dynamic performances of $Ti_{0.25}V_{0.34}Dy_{0.01}Cr_{0.1}Ni_{0.3}$ hydrogen storage electrode

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Abstract

Crystal structure and some dynamic performances of $Ti_{0.25}V_{0.34}Dy_{0.01}Cr_{0.1}Ni_{0.3}$ hydrogen storage electrode alloy have been investigated by XRD, FESEM-EDS, TEM and EIS measurements. The result shows that the alloy is mainly composed of V-based solid solution phase with body-centered-cubic structure and mono-crystal Ni_3Ti phase with hexagonal structure (Space grope: P63/mmc), and it was first observed as TiNi-based secondary phase. The higher charge transfer resistance, higher apparent activation energy and lower hydrogen diffusion coefficient are reasons for the poor electrochemical activity of the dehydriding kinetics of Ti-V-Cr-Ni hydride alloy.

Keywords: Hydrogen storage electrode alloy; Ni-MH battery; V-Based solid solution

Among all hydrogen storage alloys, AB_2 type alloys and bcc solid solution alloys are considered as the potential candidates for their larger hydrogen capacity, and it has been paid much attention for V-based solid solution alloys such as laves phase related bcc solid solution, but they have not been used for any practical application so far [1–3]. As reported by Tsukahara *et al.* [4], V-Ti-Cr solid solution alloy has a much larger hydrogen storage capacity, but almost no electrochemical activity in KOH electrolyte. The coexistent of TiNi-based secondary phase was considered to have electrochemical catalytic activity and act as a micro-current collector and as an electrochemical catalyst [5]. The secondary phase may provide an effective pathway for solving the problem of the unfavorable dynamic properties of V-based solid solution alloy. In this paper, microstructure and some dynamic parameters of $Ti_{0.25}V_{0.34}Dy_{0.01}Cr_{0.1}Ni_{0.3}$ electrode alloy have been investigated.

1. Experimental

$Ti_{0.25}V_{0.34}Dy_{0.01}Cr_{0.1}Ni_{0.3}$ alloy is prepared by arc-melting the component metals on an water cooled copper hearth under argon and re-melted for three times to ensure the homogeneity. The crystal structure of the alloy is investigated by X-ray diffraction (CuKa, Si internal standard) on Rigaku D/max 2500pc X-ray diffraction meter using JAD5

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software, the microstructure and the phase compositions of the alloy are measured by FESEM-EDS analysis on XL30 ESEM FEG Scanning Electron Microscope and by TEM analysis on JEM-2010 Transmission Electron Microscope.

The electrochemical measurements are performed in a half-cell system, and the measurement was similar to those described in our previous work [3]. To investigate the dehydriding kinetics parameters of Ti-V-Cr-Ni hydride alloy, the electrochemical impedance spectroscopy (EIS) has been used for determining the charge-transfer resistance (R_T) using Solartron SI1187 Electrochemical Interface with 1255B Frequency Response Analyzer and ZPLOT electrochemical impedance software. According to the analysis model proposed by Kuriyama *et al*. [6], R_T can be calculated by using least-square method, and the exchange current density (I_0), the diffusion coefficient of hydrogen (D) in the bulk of the alloy and the apparent energy ($\Delta_r H$) can be calculated from the following formulation (1), (2) and (3) [6–7], respectively, where R, T and F have their general meanings, δ means the Warburg coefficient in the EIS, C_0 means the original concentration of hydrogen in the alloy electrode when the EIS is determined.

$$I_0 = \frac{RT}{FR_T} \quad (1)$$

$$\delta^2 = \frac{R^2T^2}{2^n 4F^4 D C_0^2} \quad (2)$$

$$\lg\left(\frac{T}{RT}\right) = -\frac{\Delta_r H}{2.303RT + A} \quad (3)$$

2. Results and discussion

Fig. 1 shows the XRD pattern of $Ti_{0.25}V_{0.34}Dy_{0.01}Cr_{0.1}Ni_{0.3}$ electrode alloy synthesized by arc melting. It can be found that the alloy has single V-based solid solution phase with body-centered-cubic (bcc) structure. The lattice parameter and the cell volume of the bcc phase are 0.2979 nm and 0.0264 nm^3, respectively.

Fig. 2 shows the FESEM micrographs of $Ti_{0.25}V_{0.34}Dy_{0.01}Cr_{0.1}Ni_{0.3}$ electrode alloy. It is obvious that the alloy is composed of V-based solid solution phase with dendritic shape and a continuous TiNi-based secondary phase with networked shape surrounding the dendrite. The phase composition of the alloy has been semi-quantitatively analyzed with EDS which is also shown in Fig. 2 and the results are shown in Table 1. It can be seen that V-based solid solution phase is mainly composed of V and Cr, while TiNi-based secondary phase is mainly composed of Ti and Ni.

TEM has been used to analysis the compositions of the phase. Fig. 3 (a) shows that the alloy is composed of V-based solid solution phase with bcc structure, and it is coincided well with that of FESEM. It should be pointed out that mono-crystal Ni_3Ti with hexagonal structure (a = 0.5093; c = 0.8320; Space grope: P63/mmc) has been detected in TiNi-based secondary phase as shown in Fig. 3 (b). The higher Ni content is beneficial for the alloy to improve electrochemical activity of V-based solid solution phase.

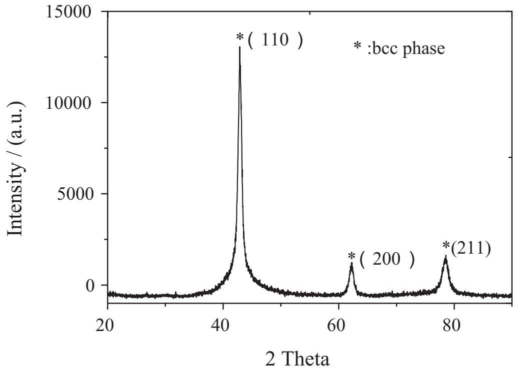

Fig. 1. X-ray diffraction pattern of $Ti_{0.25}V_{0.34}$ Dy $_{0.01}Cr_{0.10}Ni_{0.30}$ electrode alloy.