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Investigation on gaseous and electrochemical hydrogen storage performances of as-cast and milled $\text{Ti}_{1.1}\text{Fe}_{0.9}\text{Ni}_{0.1}$ and $\text{Ti}_{1.09}\text{Mg}_{0.01}\text{Fe}_{0.9}\text{Ni}_{0.1}$ alloys

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ABSTRACT

The AB-type $\text{Ti}_{1.1}\text{Fe}_{0.9}\text{Ni}_{0.1}$ (Mg_0 for short) and $\text{Ti}_{1.09}\text{Mg}_{0.01}\text{Fe}_{0.9}\text{Ni}_{0.1}$ ($\text{Mg}_{0.01}$ for short) alloys were fabricated by vacuum induction melting and mechanical milling. The effects of partly substituting Ti with Mg and/or mechanical milling on the structure, morphology, gaseous thermodynamics and kinetics, and electrochemical performances were studied. The results reveal that the as-cast Mg_0 alloy contains the main phase TiFe and a small number of TiNi_3 and Ti_2Ni phases. Substituting Ti with Mg and/or mechanical milling results in the disappearance of the secondary phases. The discharge capacities of the as-cast Mg_0 and $\text{Mg}_{0.01}$ alloys are 12.6 and 8.8 mAh g^{-1} , which increase to 52.6 and 80.4 mAh g^{-1} after 5 h of mechanical milling. By milling the as-cast alloy powders with carbonyl nickel powders, they are greatly enhanced to 191.6 mAh g^{-1} for the $\text{Mg}_0+7.5$ wt% Ni alloy and 205.9 mAh g^{-1} for the $\text{Mg}_{0.01}+5$ wt% Ni alloy at the current density of 60 mA g^{-1} , respectively. The values of dehydrogenation enthalpy (ΔH_{des}) and dehydrogenation activation energy ($E_{\text{des}}^{\text{des}}$) are very small, meaning that the thermal stability and the desorption kinetics of the hydrides are not the key influence factors for the discharge capacity. The reduction of the particle size and the generation of the new surfaces without oxide layers have slight improvements on the discharge capacity, while the enhancement of the charge transfer ability of the surfaces of the alloy particles can significantly promote the electrochemical reaction of the alloy electrodes.

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Introduction

The end of fossil fuel era will be an inevitable consequence. It has become the general trend and the common aspiration of

people across the world to research and use clean energy. Especially in transportation, there are increasing new energy vehicles on the streets [1]. At present, most of hybrid electric vehicles take nickel metal hydride (Ni-MH) batteries as auxiliary power, such as Toyota Prius, and the performances

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of Ni-MH batteries largely decide their market prospects. It is well known that the major performances of a Ni-MH battery basically depends on its negative electrode material, viz., hydrogen storage material [2,3]. However, although many hydrogen storage materials have been discovered, none of them is satisfactory due to the low discharge capacity, poor cycle life and so on [4–11]. TiFe-based hydrogen storage alloys have been extensively studied in recent years due to the relatively high hydrogen storage capacity, moderate working temperature and cheap raw materials [12–22]. Especially the theoretical electrochemical capacity of TiFe alloy is up to 512 mAh g⁻¹, nearly 1.4 times that of LaNi₅ alloy, and the cost of raw materials is less than one-third of that of LaNi₅ alloy.

Unfortunately, the actual discharge capacity is very small for TiFe alloy, which has restricted its application in the Ni-MH battery. Jankowska et al. [23] reported that the discharge capacities of the as-cast and milled TiFe alloys are 0 and 64 mAh g⁻¹ at 4 mA g⁻¹ discharge current density. Jurczyk et al. [24] synthesized TiFe_{0.25}Ni_{0.75} alloy by mechanical milling and annealing, and the discharge capacity achieves to 155 mAh g⁻¹ at 40 mA g⁻¹ discharge current density. Anani et al. [25] considered that the newly added grain boundaries can enhance the diffusion ability of the hydrogen atoms in the alloys.

Most of the researches draw a conclusion that the poor discharge capacity is due to the fact that Ti is easy to be oxidized and the formed oxides cover the surfaces of the alloy electrode, which further inhibit the electrochemical reactions [23,24]. However, the key influence factor for the discharge capacity is not clear. And the discharge capacities of the existing alloys are very small even at low current density, such as 4 and 40 mA g⁻¹. In this paper, Fe was substituted by Ni partly and then the trace amounts of Mg additives were added into the alloys in order to improve the discharge capacity. Mechanical milling with different proportions of carbonyl nickel powders (0, 2.5, 5, 7.5 and 10 wt%) was used to enhance the charge transfer ability of the alloys. The relationship between the structure, morphology, gaseous thermodynamics and kinetics and electrochemical performances of the alloys were investigated in detail. The influence factors for the discharge capacity were analyzed one by one. Through this work, the discharge capacity of the as-milled (5 h) Mg_{0.01}+5 wt % Ni alloy reaches to 205.9 mAh g⁻¹ at the current density of 60 mA g⁻¹. And the key influence factor for the discharge capacity of the alloys was given.

Experimental

The as-cast Ti_{1.1}Fe_{0.9}Ni_{0.1} and Ti_{1.09}Mg_{0.01}Fe_{0.9}Ni_{0.1} alloys were prepared by melting the raw materials using a vacuum induction furnace. For ease of description, this paper uses Mg₀ and Mg_{0.01} to represent the Ti_{1.1}Fe_{0.9}Ni_{0.1} and Ti_{1.09}Mg_{0.01}Fe_{0.9}Ni_{0.1} alloys, respectively. Due to the fact that the melting point and boiling point of Mg are far below than Ti, Fe and Ni, the volatilization loss of Mg will be severe in the process of melting. For reducing the loss, helium gas of 0.04 MPa was filled into the furnace, and the heating power was adjusted to short the melting time as much as possible. A part of the cast ingot was chosen as sample and crushed into powders with

the average particle size of 70 μm. The obtained powders were milled with the different proportions of carbonyl nickel powders (0, 2.5, 5, 7.5 and 10 wt%; 0.5–2.2 μm) for 9.5 h with the total weight of 5 g, respectively. The weight ratio of ball to powder was 40:1. The powder specimens were milled clockwise for 30 min firstly, resting for 30 min, and then milled counterclockwise for 30 min at the rotation speed of 350 r min⁻¹.

X-ray diffractometer (XRD) (D/max/2400) was used to analyze the phase composition of the experimental alloys, and the test parameters were set as follow: 160 mA, 40 kV and 10° min⁻¹ respectively, performing with CuK_{α1} radiation filtered by graphite. Field Emission Transmission Electron Microscopy (FETEM) (TecnaiG2 F30) was used to observe the crystal structure of the experimental alloys, and working voltage was set to 200 kV. Selected area electron diffraction (SAED) was exploited to characterize the crystalline state.

An automatically controlled Sieverts apparatus was used to measure the gaseous hydrogen storage properties. The sample mass for every measurements run was 1 g fitted in a cylindrical reactor. The alloy was activated firstly by five hydriding and dehydriding cycles at 653 K. The pressure-composition-isotherms (P-C-T) and kinetics of the activated samples were tested at 313, 333 and 353 K, respectively. The test temperature was controlled by a furnace with the accuracy of ±1 K. In the P-C-T measurement, the time for the system to attain thermodynamic equilibrium was 60 min and the maximum hydrogen pressure was 3 MPa. In the kinetics measurement, the initial hydrogen pressure in the cylindrical reactor was set to 3 and 1 × 10⁻⁴ MPa for the hydriding and dehydriding process, respectively.

A mixture of 0.2 g alloy powders and 0.8 g carbonyl nickel powders was pressed into a mould to form the φ15 mm round electrode pellet at a pressure of 35 MPa for 5 min. The electrode pellet was sandwiched within two foamed Ni plates about 20 × 20 mm². The two foamed Ni plates were welded together firstly, and then a Ni strip was welded on one side of it to form a metal hydride electrode. The metal hydride electrode, sintered Ni(OH)₂/NiOOH counter electrodes as well as a Hg/HgO reference electrode constituted a tri-electrode open cell which was infused with 6 mol L⁻¹ KOH electrolyte. The voltage between the metal hydride electrode and the Hg/HgO reference electrode was defined as the discharge voltage. According to the general standard, the metal hydride electrode was charging to the critical saturation, standing for 15 min, and then discharging to -0.500 V at 303 K and the certain current density of 60 mA g⁻¹.

Results and discussion

Microstructure characterization

Fig. 1 shows the XRD patterns of the as-cast and milled (5 h) Mg₀ and Mg_{0.01} alloys at different states. There are the major phase TiFe phase corresponding to the CsCl structure with Pm3 m space group and a small number of TiNi₃ and Ti₂Ni phases in the as-cast Mg₀ alloy [26]. The secondary phases disappear and the alloys become TiFe single-phase structure after substituting Ti with the trace amounts of Mg additives

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