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Effect of polyaniline on hydrogen absorption–desorption properties and discharge capacity of AB_3 alloy

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Abstract

A series of AB_3/PANI composites were prepared by adding polyaniline (PANI) into $La_{0.7}Mg_{0.25}Ti_{0.05}Ni_{2.975}Co_{0.525}$ (AB_3) hydrogen storage alloy, which was prepared by magnetic levitation melting, and the composites were investigated by XRD and SEM. The effects of PANI concentration on the hydrogen absorption–desorption properties and discharge capacities of AB_3 alloy were systematically studied by P–C–T isotherms and LAND battery test system, respectively. The results indicated that the addition of PANI did not change the hydrogen absorption capacity of AB_3 alloy distinctly, while the hydrogen desorption plateau pressure of AB_3 alloy decreased firstly, and then increased with the increase in the PANI concentration, the minimum plateau pressures of 0.022, 0.1, 0.321 and 0.55 MPa were obtained with PANI concentration of 2 wt% at 25, 50, 80 and 100 °C, respectively. It was theoretically verified by the changes in enthalpy and entropy of AB_3/PANI hydrides dehydrogenation which were calculated by Van't Hoff equation. In the present paper, the phenomenon that PANI improved the hydrogen absorption kinetics of AB_3 alloy was found; the influence of PANI concentration on hydrogen absorption kinetics of AB_3 alloy was more apparent at higher temperature. The activation energies of dissolved hydrogen in AB_3/PANI hydrides were calculated from hydrogen absorption kinetics and the Arrhenius equation. LAND experiments demonstrated that, the AB_3/PANI electrodes composites possessed higher cycling discharge capacity retention rates than AB_3 electrode alloy.

Keywords: AB_3/PANI composite; Hydrogen storage capacity; Hydrogen absorption kinetics; Thermodynamics; Discharge capacity

1. Introduction

As a hydrogen absorption media for metal alloys, polymer attracted much attention in the last several years [1]. Uemura and coworkers [2] reported the effect of polystyrene on the hydrogen absorption properties of $LaNi_5$ alloy. They found that the hydrogen absorption capacity of the alloy was not influenced by the encapsulating treatment. Tinge [3] also obtained the same conclusion by studying the hydrogen absorption and desorption kinetics of the polyethylene/$LmNi_4$ (Lm = lanthanide mixture).

Recently, a study on the mechanism of hydrogen storage in polymer was reported by Schmidt [4], who considered that polymer could improve the hydrogen movement in metal alloy. And then, the experimental results of Isobe and Yamauchi et al. [5,6] showed that addition of certain polymer could increase the hydrogen absorption capacity of Pt or Pd nanoparticles. PANI, as a normal polymer, does not have the hydrogen storage capacity itself [7], but it could accelerate the hydrogen absorption kinetics of AB_2 alloy [8]. So it would be interesting to systematically study the effect of PANI on hydrogen absorption–desorption properties of AB_3 alloy, a typical hydrogen storage alloy. In the present work, PANI was added

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into AB_3 alloy to improve unfavorable properties such as hydrogen absorption kinetics of AB_3 alloy. The effect of PANI concentration on the hydrogen absorption–desorption and kinetic properties of AB_3 alloy was investigated by a P-C-T apparatus. The discharge capacities of AB_3/PANI electrodes composites were also studied in this paper.

2. Experimental

2.1. Sample preparation

PANI was prepared by $(NH_4)_2S_2O_8$ oxidation of aniline in 2 M HCl aqueous solution [9]. Before compounding with AB_3 alloy, it was dried at 100 °C under vacuum for 4 h to wipe off water.

The AB_3 alloy was prepared by magnetic levitation melting under argon atmosphere. The alloy button was crushed into fine powders below 200 meshes.

2.2. Preparation and characterization of AB_3/PANI composites

The AB_3 alloy below 200 meshes was activated by 4 MPa hydrogen at room temperature for three times [10], then the activated AB_3 alloys were compounded with 0, 1, 2, 4 wt% (to AB_3 alloy) PANI, respectively, by hand milling for 30 min. The AB_3/PANI composites were characterized by XRD (Rigaku D/max-2500, Cu Kα, 40 kV, 250 mA) and scanning electron microscopy (JSM-6360LV).

2.3. Hydrogen pressure-composition isotherm and kinetics studies

Hydrogen absorption–desorption behaviors of AB_3/PANI composites were measured using a Severts-type apparatus up to a hydrogen pressure of 4 MPa similar to our previous work [11]. Repeated measurements of absorption–desorption sequence were carried out in the temperature range of 25–100 °C. The absorption kinetics data were automatically collected by recording the change in pressure as a function of time at constant temperature.

2.4. Charge–discharge capacity

The charge–discharge measurements were performed on a LAND automatic battery testing system as described elsewhere [12,13]. The tested electrodes were fabricated by mixing 0.1 g AB_3/PANI composites with 0.3 g electrolytic Ni powder. The above mixture containing AB_3/PANI composite and Ni powder was pressed into a pellet under a pressure of 30 MPa. Both sides of the pellet were coated with two foam nickel sheets, then pressed at 10 MPa and tightly spot-welded. A nickel lead wire was attached to this pressed foam nickel sheet by spot welding. The NiOOH/$Ni(OH)_2$ electrode and Hg/HgO electrode were used as counter and reference electrode, respectively. The electrolyte was 6 M KOH aqueous solution. The electrodes were charged for 3 h at a current density of 300 mA g^{-1}, rested 5 min and then discharged to −0.6 V versus Hg/HgO electrode at a current density of 100 mA g^{-1}. The measurements were carried out at room temperature of 25 °C.

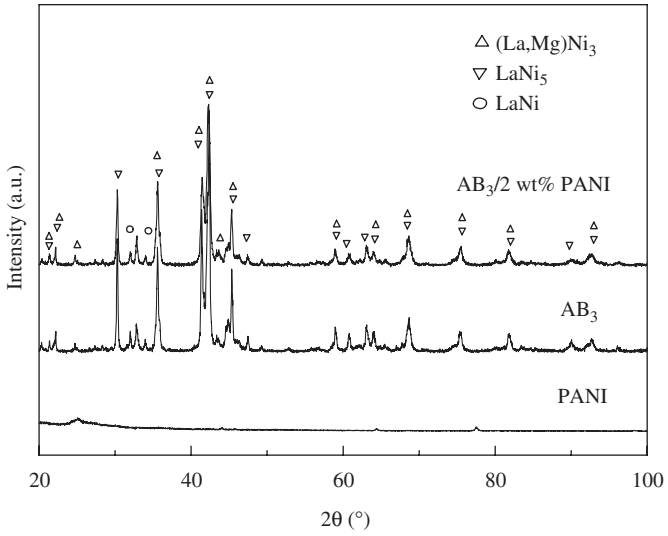

Fig. 1. XRD patterns of the AB_3/PANI composites.

3. Results and discussion

3.1. Crystal structure

Fig. 1 shows the X-ray diffraction patterns for the AB_3 alloy, PANI and AB_3/2 wt% PANI composite. For PANI, a broad Bragg peak was observed at approximately 25°(2θ), which confirmed that the prepared PANI was amorphous. As to samples of AB_3 alloy and AB_3/2 wt% PANI composite, two main phases, i.e. the (La, Mg)Ni_3 phase with $PuNi_3$-type rhombohedral structure and $LaNi_5$ phase with $CaCu_5$-type hexagonal structure were observed in their XRD patterns [14,15]. However, in the XRD pattern of AB_3/2 wt% PANI composite, the PANI phase was not observed for its low intensity. SEM images of (a) AB_3 (< 200 meshes, without other treatment), (b) AB_3/0 wt% PANI composite (with activation and hand milling), (c) AB_3/2 wt% PANI composite are shown in Fig. 2. It was found that the average particle size of these materials reduced with the treatment of activation and hand milling, the average particle size of AB_3/2 wt% PANI composite was the smallest, about 25 μm.

3.2. P–C–T isotherms

Hydrogen absorption–desorption isotherms and the maximum hydrogen storage capacities of AB_3/PANI composites at different temperatures (25, 50, 80 and 100 °C) are shown in Fig. 3 and Table 1, respectively. It can be seen that at 25, 50, 80 and 100 °C, the maximum hydrogen absorption capacities of AB_3 alloy were the highest, and they decreased with the increase in PANI concentration. This result was in good agreement with that observed in Ref. [8], because PANI does not