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Effect of Preparation Technique on Microstructure and Hydrogen Storage Properties of $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ Alloys

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$LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloy was prepared by vacuum induction melting and melt-spinning. The effects of different preparation techniques of the as-cast, cast then annealed, as-spun and spun then annealed alloys on the microstructure and hydrogen storage properties were investigated. The results indicated that the non-$CaCu_5$ phases in the alloy became tinier and more dispersive after annealing or melt-spinning compared to those of the as-cast one. But in the spun then annealed alloy, the non-$CaCu_5$ phases disappeared and only a single-phase with $CaCu_5$ type structure was found. For all the alloys, the cell volume was increased in an order of as-cast < spun then annealed < cast then annealed < as-spun, and the change of plateau pressure showed the opposite trend with that of the cell volume. The plateau could be flattened after melt-spinning or annealing, and the spun then annealed alloy showed the minimum plateau slope. The absorption kinetics of the alloy was promoted after melt-spinning or annealing. It is suggested that the change in cell volume and compositional homogeneity resulting from different preparation techniques contribute to the difference of the hydrogen storage properties of the investigated alloys.

1. Introduction

Hydrogen energy is one of the ideal solutions to both energy crisis and environmental pollution, which have become two serious threats to the development of the human society nowadays. Metal hydride is a safe and cost-effective candidate for hydrogen storage[1–11]. Among various metal hydrides, $LaNi_5$ is a superior hydrogen storage alloy, which has been comprehensively investigated for its high capacity, easy activation, and fast kinetics[2–5]. Substituting different elemental species into the Ni lattice sites has been widely used to acquire novel hydrogen storage properties for $LaNi_5$-based alloys. Due to their low plateau pressures, long cycling life and good tolerance to impurities, which are required in some special situations, several investigations[2–9] concerning on the hydrogen storage properties of La–Ni–Al, La–Ni–Mn and La–Ni–Al–Mn have been reported.

The plateau pressure and flatness of PCT curve (pressure-composition isotherm) of hydrogen storage alloys are important for their practical applications. As known[1,2], annealing or melt-spinning is effective in flattening the plateau regions, and both of them tend to alleviate the segregation in the alloys. However, annealing makes an equilibrium state and removes the lattice defects, while melt-spinning makes a non-equilibrium state and impels the alloys to form more lattice defects and grain boundaries[2–4]. Since the difference in the microstructure could directly affect the whole hydrogen storage properties of the alloys, it is necessary to prepare the alloy by various techniques, and then characterize their effects on microstructure and hydrogen storage properties.

Our previous work[5–7] revealed that $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloy demonstrated an outstanding potential as a hydrogen storage alloy. In the present work, the microstructure, PC-isotherms and hydrogen absorption kinetics of the as-cast, cast then annealed, as-spun, and spun then annealed$LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloys were studied to evaluate the effect of preparation technique on the microstructure and hydrogen storage properties of the $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloy.

2. Experimental

The experimental $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloy was prepared by a vacuum induction furnace under argon atmosphere. The purities of the starting materials were La 99%, Ni 99.9%, Al 99.7% and Mn 99.7%. Afterward, one part of the as-cast alloy was annealed at 1223 K for 6 h under argon atmosphere, while the other part was melt spun by a single-roller melt-spun equipment at a roller surface velocity of 17.3 m/s under argon atmosphere, and then one part of the as-spun alloy was annealed at 1223 K for 3 h under argon atmosphere. The hydrogen storage properties of $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloy with

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different states were determined using a Sieverts-type apparatus. The initial activation for the alloys was performed by exposing about 1.4-g sample to 1.5-MPa hydrogen at 413 K after evacuation for 0.5 h by a rotary pump. After six cycles of hydrogen absorption/desorption, the sample was fully activated. Hydrogen absorption/desorption PC isotherms and absorption kinetics were obtained in a temperature range of 413–473 K by the conventional volumetric method using the commercial hydrogen with a purity of 99.999%. Hydrogen absorption kinetics data were collected as a function of time at an initial pressure of 2 MPa by recording the change in pressure. The slope factor is described as $S_f = (\mathrm{d}\ln P)/\mathrm{d}(H/M)$, where P is the equilibrium pressure and H/M is the hydrogen content expressed as atomic ratio.

The crystal structure of the samples was determined by X-ray diffraction (XRD) with CuK_α radiation. The cross-section morphology and elemental composition were studied by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS).

3. Results and Discussion

3.1. Structure characteristics

SEM images of the cross-section of the as-cast and melt-spun $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloys before and after annealing are shown in Fig. 1. The images indicated that the grains of the as-cast alloy are very coarse, while melt-spinning made the grain size decrease obviously. These results are in good agreement with previous reports[8,9] that the grain size of the as-spun alloy is very small, while it grows up obviously after annealing.

Figs. 2 and 3 show the phase distribution and composition of $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloys prepared by different techniques, and the phase constituents analyzed by EDS are listed in Table 1. It can be found that the as-cast alloy consisted of a matrix phase: $LaNi_5$ phase (A1), and three second phases: $LaNi_2$ phase (B1), $LaNi_3$ phase (C1) and AlNi phase (D1). After annealing or melt-spinning, the second phases became tiny and dispersive and the $LaNi_2$ phase changed into LaNi phase (B2, B3). For the spun then annealed alloy, the second phases disappeared, and only a single $LaNi_5$ phase (A4) was observed. This reveals that the annealing or melt-spinning process effectively improved the compositional homogeneity of the alloy. Previous study[2,10,11] also found that the annealing or melt-spinning significantly changed the microstructures of the alloys, decreased the amount of the secondary phase, and produced both homogenous phase structure and alloy composition.

Fig. 4 shows the XRD patterns of $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloys prepared by different techniques, where only the diffraction peaks from the crystal planes of the $CaCu_5$ type hexagonal structure phase can be clearly resolved. The lattice parameters, cell volumes and lattice strains (e) of the $CaCu_5$ phase were obtained by using JADE software[12], and listed in Table 2. The data showed that the lattice parameters and cell volumes of the as-cast alloy remarkably increased after annealing or melt-spinning, while those of the as-spun alloy slightly decreased after annealing. The cell volume was increased in an order of as-cast < melt-spun then annealed < cast then annealed < as-spun. This is also consistent with previous studies that the unit-cell dimensions of the alloys could be increased after annealing or melt-spinning[13,14], however, the unit-cell dimensions of the melt-spun alloy decreased after annealing at 1213 K[15].

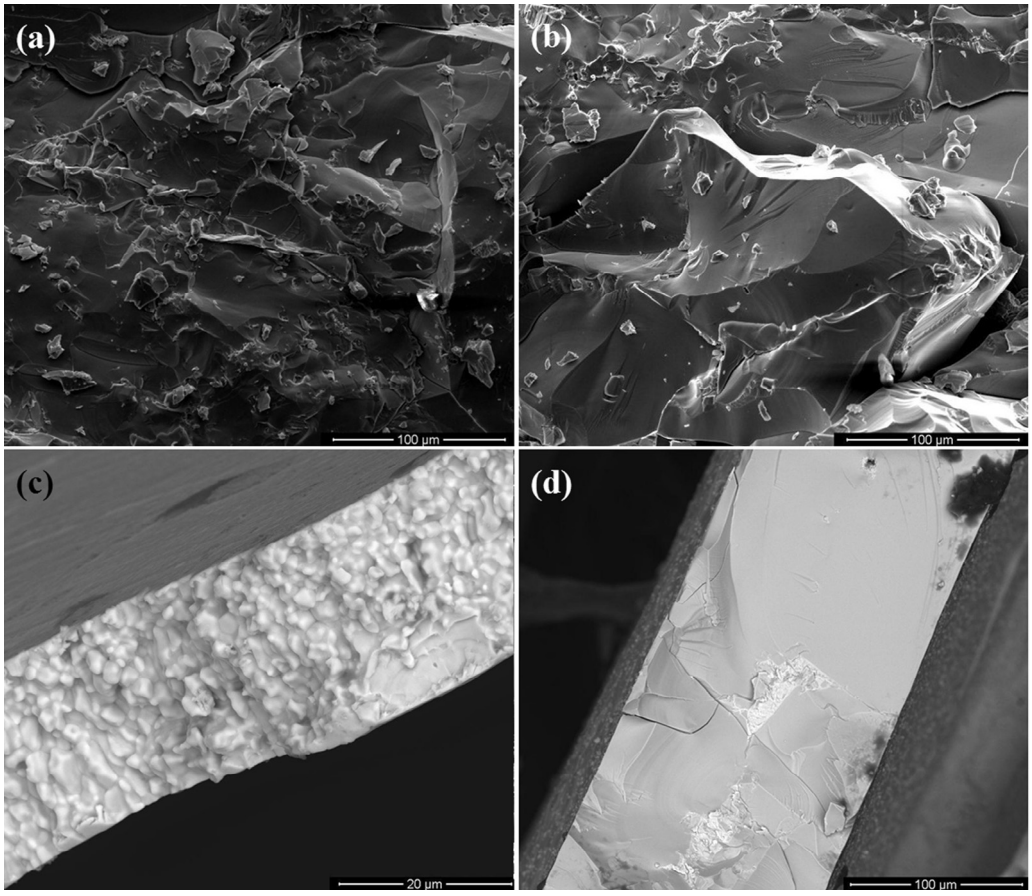

Fig. 1. Cross-section of the $LaNi_{3.8}Al_{1.0}Mn_{0.2}$ alloys prepared by different techniques: (a) as-cast; (b) cast then annealed at 1223 K; (c) as-spun; (d) spun then annealed at 1223 K.