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Hydrogenation thermokinetics and activation behavior of non-stoichiometric Zr-based Laves alloys with enhanced hydrogen storage capacity

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ABSTRACT

$Zr_{0.9-x}Ti_{0.4+x}V_{1.7}$ (x = 0, 0.1) non-stoichiometric alloys are designed and expected to show improved hydrogen storage capacities of Zr-based Laves phase alloys. The samples are synthesized by arc melting followed by two different processing techniques: annealing and melt-spinning. Phase constituent and microstructure investigations reveal the multiphase structures containing C15-Laves type ZrV_2, V- and Zr-based solid solutions for the annealed alloys and melt-spun ribbons. The content of ZrV_2 decreases but the unit cell volume of ZrV_2 increases with increasing Ti content. Activation behavior and hydrogenation kinetics at different temperatures of the annealed and melt-spun samples were studied. At 25 °C, the hydrogen absorption capacity of $Zr_{0.8}Ti_{0.5}V_{1.7}$ reaches 2.83 wt% H. The apparent activation energies of the fast hydrogen absorption stage (α, α+β regions) are calculated to be 2–5 kJ/mol. Melt-spun ribbons exhibit higher hydrogen absorption rate and smaller hydrogen storage capacities than the annealed alloys in the initial cycle. The surface and sub-surface chemical compositions are analyzed by XPS to illustrate the influence of composition of the alloys on activation behavior. Hydrogen absorption/desorption PCT curves of the annealed samples between 400 and 550 °C were measured and allowed to derive corresponding thermodynamics parameters. The higher hydride stability of the $Zr_{0.8}Ti_{0.5}V_{1.7}$ based hydride is related to its larger unit cell volume and higher α-Zr content as compared to $Zr_{0.9}Ti_{0.4}V_{1.7}$.

1. Introduction

Hydrogen is considered to be a clean energy carrier in future society. The safe and efficient hydrogen storage is the vital link in the development of hydrogen energy economy. Metal hydrides have been extensively studied and the ideal compounds for gas storage applications are expected to present high hydrogen capacity, fast kinetics, good reversibility and cyclic stability, moderate plateau pressure and low hysteresis [1,2]. Among hydrogen storage alloys, Zr-based AB_2 intermetallics find applications in Ni–MH batteries, hydrogen isotope separation, gas purification, etc [3]. The typical Laves phase alloy ZrV_2 preserves the ultralow equilibrium pressure 10^{-8} bar at room temperature which is suitable for low hydrogen pressure applications, especially for the extraction of hydrogen (through absorption) from a mixture of gases [4,5]. Hydrogen storage capacity of ZrV_2 has been reported to be 4.8 H/f.u. (2.43 wt%) at 1 atm hydrogen pressure and 5.5 H/f.u. (2.77 wt%) at 52 atm hydrogen pressure [6]. The saturated deuteride ZrV_2D_6 has been synthesized at pressure of about 1 bar and structurally characterized in temperature range 110–210 K [7]. However, the stability of hydrides ZrV_2H_x is too high and the hysteresis between hydrogen absorption and desorption is obvious [8].

Much efforts have been devoted to improve the hydrogenation properties of Zr-based AB_2 alloys, in which the multi-element alloying is the most efficient one. Several elements such as Al, Ni, Ti, Fe are doped into ZrV_2 alloy separately or together. The substitution of Ni at V side in $Zr(V_{1-x}Ni_x)_2$ (x = 0.02–0.25) reveals that the unit cell volume decreases linearly with increasing Ni content, accordingly, the hydrogen absorption capacity decreases (from 2.3 wt% to 2.0 wt%) and equilibrium pressure increases [9]. The attempt of substituting V by light weight element Al in $Zr(Al_xV_{1-x})_2$ shows the increasing content of Al destabilizes the bulk hydrogen absorption and large substituted Al quantities inhibit hydrogen absorption [10]. Titanium is also effective to modify ZrV_2 alloy, as Ti-doped near AB_2-type Zr-Ti-V series alloys show improved hydrogenation kinetics, lower hysteresis and ultralow equilibrium

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pressure. But the hydrogen storage capacities under 0.5 atm hydrogen pressure are around 2.1–2.4 wt% which are smaller than that of ZrV_2 [11–13]. Melt-spinning technique has been widely applied to Mg-, Ti- and Zr-based alloys to explore the effect of rapid solidification on microstructures, electrochemical and hydrogen storage properties [14–18]. Improvement on hydrogen absorption/desorption properties via the synthesis of nanocrystalline structures has been achieved. The large number of interfaces and grain boundaries available in the nanocrystalline materials give preferential pathways for hydrogen diffusion and accelerate the hydrogen absorption. However, the effect of melt-spinning technique on hydrogen storage capacity of bulk alloys is inconsistent [15,19–21]. In general, hydrogen storage capacity and kinetics of Zr-based Laves phase alloys are expected to be improved simultaneously and it is attractive for researchers to explore the effective pathways and corresponding mechanisms about that.

Understanding the formation condition of multiphase alloys and the effect of multiphase on hydride properties from previous works gives us an inspiration that adjusting the stoichiometry ratio on the base of AB_2-type $Zr_{0.9}Ti_{0.1}V_2$ can probably improve the hydrogen storage capacity. In this work, high Ti-doped $Zr_{0.9-x}Ti_{0.4+x}V_{1.7}$ ($x = 0, 0.1$) alloys are designed. Microstructure, phase constituent, activation behavior and hydrogenation kinetics of annealed and melt-spun samples are comparatively studied to reveal the decisive factors affecting the hydrogenation properties and the structure-function relationship of Zr-based hydrogen storage alloys. The apparent activation energies of the fast hydrogen absorption stage are calculated. The surface and sub-surface chemical analysis by XPS is adopted to discuss the influence of compositions on activation behavior.

2. Experimental procedures

$Zr_{0.9-x}Ti_{0.4+x}V_{1.7}$ ($x = 0, 0.1$) alloys were prepared by arc melting in water-cooled copper crucible under high purity argon atmosphere. The ingots were turned over and re-melted 3 times to ensure the homogeneity. Half of the ingots was annealed at 1000 °C for 168 h in quartz tube under vacuum of 6×10^{-3} Pa followed by furnace cooling to room temperature. The other half of the ingots was re-melted in a quartz tube by induction melting and spun under argon atmosphere on a rotating copper wheel with a linear velocity of 40 m/s. The ribbons with dimensions of about 50 μm in thickness, 5 mm in width and 10–80 mm in length were obtained.

The phase compositions of the alloys were determined by a DX-2700 X-ray diffractometer (XRD) using Cu K_a radiation. With a step scanning mode (step width 0.03, counting time 2s), the diffraction data were collected at room temperature between 20° and 80° (2θ).The microstructure of each sample was investigated by a scanning electron microscope (SEM) using secondary electron imaging. The elemental distribution was determined by an energy dispersive spectrometer (EDS) using point scan mode.

To characterize the compositions and valence on surface and subsurface of air exposed $Zr_{0.9}Ti_{0.4}V_{1.7}$ alloy before hydrogenation, X-ray photoelectron spectrometer (XPS) using Al K_α excitation was employed. The base pressure in the chamber was 5×10^{-6} Pa. The analyzer pass energy was 100 eV for survey spectra and 200 eV for high-resolution spectra (step width 1 eV, counting time 150 m). The parameters of the Ar-ion gun are: 2 kV beam, 2 μA sample current, depth by 0.28 nm per second and the etching time is 60 s. The binding energy (BE) scale was calibrated by measuring the carbon (C 1s, 284.6 eV) core level signal before and after the measurements.

Hydrogen storage characteristics including the P-t and PCT curves for each sample (~0.2 g) were obtained from a Sievert type apparatus. Prior to the measurements, the samples were activated by heating the chamber to 500 °C and pumping for 30–40 min to 2×10^{-3} Pa in order to create a clean surface free from surface contaminations. All measurements were conducted in the temperature range 400–550 °C under isothermal conditions and at hydrogen pressures of less than 50 kPa. Samples were prepared for the next measurement cycle by degassing at 550 °C, under vacuum of 2×10^{-3} Pa. Pressure drop was measured as a function of time and converted to the weight percent (wt.% H) of hydrogen absorption capacity.

3. Results and discussion

3.1. Phase constituents and microstructures

XRD patterns of the annealed and melt-spun $Zr_{0.9-x}Ti_{0.4+x}V_{1.7}$ ($x = 0, 0.1$) are shown in Fig. 1(a) and (b), respectively. Diffraction peaks of the annealed alloys (Fig. 1(a)) reveal the multiphase structure of C15-type Laves phase ZrV_2, α-Zr and V-BCC. A significant amount of zirconium and vanadium solid solutions are generated from the incomplete peritectic reaction during non-equilibrium solidification process, and the annealing treatment of 1000 °C/168 h can not eliminate them [12,22]. The phase

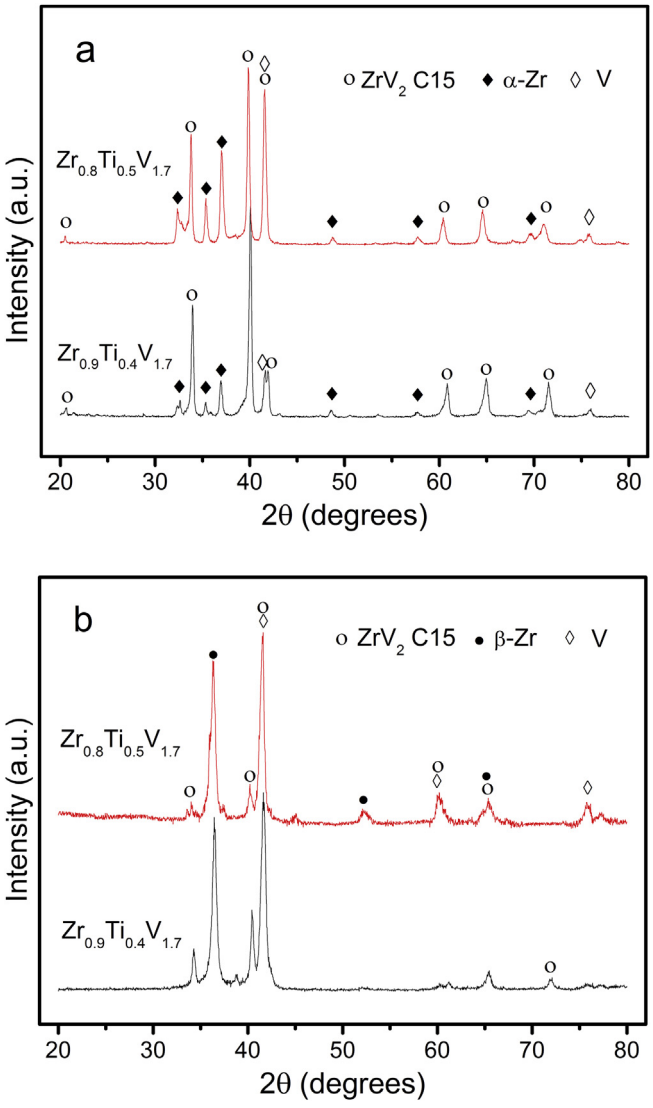

Fig. 1. XRD patterns of annealed (a) and melt-spun (b) $Zr_{0.9-x}Ti_{0.4+x}V_{1.7}$ ($x = 0, 0.1$).