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Microstructure and hydrogen storage properties of non-stoichiometric Zr–Ti–V Laves phase alloys

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ABSTRACT

The non-stoichiometric C15 Laves phase alloys namely $Zr_{0.9}Ti_{0.1}V_x$ ($x = 1.7, 1.8, 1.9, 2.1, 2.2, 2.3$) are designed and expected to investigate the role of defect and microstructure on hydrogenation kinetics of AB_2 type Zr-based alloys. The alloys are prepared by non-consumable arc melting in argon atmosphere and annealed at 1273 K for 168 h to ensure the homogeneity. The microstructure and phase constitute of these alloys are examined by SEM, TEM and XRD. The results indicate the homogenizing can reduce the minor phases α -Zr and abundant V solid solution originating from the non-equilibrium solidification of as-cast alloys. Twin defects with $\{111\}\langle 011 \rangle$ orientation relationship are observed, and the role of defects on hydrogenation kinetics is discussed. Hydrogen absorption PCT characteristics and hydrogenation kinetics of $Zr_{0.9}Ti_{0.1}V_x$ at 673–823 K are investigated by the pressure reduction method using a Sievert apparatus. The results show the hypo-stoichiometric alloys preserve faster hydrogenation kinetics than the hyper-stoichiometric ones due to the decrease of dendritic V. The excess content of Zr_2V_3O phase decreases the hydrogenation kinetics and the stability of hydrides. In addition, the different rate controlled mechanisms during hydrogen absorption are analyzed. The effects of non-stoichiometry on the crystal structure and hydrogen storage properties of $Zr_{0.9}Ti_{0.1}V_x$ Laves alloys are discussed.

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1. Introduction

Intermetallic compounds are widely used in hydrogen storage and the purification of hydrogen isotopes. For the excellent hydrogen absorption ability, large solubility and high diffusivity for the adsorbed gases and ease of activation, AB_2 type Zr-based intermetallic compounds with C14/C15 Laves structure possess potential applications in fields of storage and separation of hydrogen and its isotopes, and have received much attention during past decades [1–5]. ZrV_2 alloy has been reported to reach the hydrogen absorption capacity 4.8 H/A at 1 atm hydrogen pressure without changing crystal structure

[6], and the value can be 5.3 H/A at 12 atm hydrogen pressure [7]. Meanwhile, ZrV_2 alloy preserves an ultra low equilibrium hydrogen pressure at room temperature for the potential applications as non-evaporable getter materials, which can upgrade and sustain the vacuum inside the cavity of vacuum-type devices. However, the shortage in hydrogen absorption kinetics and the hydrogen desorption hysteresis makes it difficult to meet the requirements of applications in the nuclear industry [8].

Many studies have been carried out to improve the activation, discharge capacity, absorption/desorption kinetics, cycle life and decrease the stability of metal hydrides of

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Zr-based AB_2 alloys by adding some alloying elements partially substituting the element in A or B site [9–11]. The work of Iwakura et al. shows that the increase of r_A/r_B value or decrease of unit cell volume in $ZrV_{2-x-y}Mn_xNi_y$ Laves phase alloys results in the decrease of the interaction between constituent metals and hydrogen and the increase of the hydrogen diffusion rate. Meanwhile, the absolute value of enthalpy change reduces which indicates the reduction of hydrides stability and improvement of hydrogen desorption [12]. Doping Ti for Zr in $(Zr-Ti)(Ni-Mn-Cr-V)$ AB_2 alloys, the smaller Ti content or the larger unit cell volume, the larger reversible absorption capacity and the lower equilibrium plateau pressure can be obtained [13]. The AB_2 type Zr–Ti–V series compounds, including the $Zr_{1-x}Ti_xV_2$ ($x = 0-0.3$) and the $ZrTi_{0.2}V_{1.8}$, show improved activation characteristics, desorption hysteresis and hydrogenation kinetics [14,15]. Proper Ti substitution for Zr is an efficient way to improve the hydrogenation kinetics comparing with the primary ZrV_2 due to the introduction of twin defects and the V BCC solid solutions. Twin defects can be preferential diffusion paths for hydrogen and the elastic stresses generated by the twins favor the nucleation of the hydrides [16]. An autocatalytic mechanism caused by V BCC solid solutions results in the acceleration of hydrogenation kinetics [15]. But Ti substitution for Zr decreases hydrogen absorption capacity. Summarize the above mentioned, the substitutions usually induce a change of the unit cell volume, phase compositions, chemical affinity to hydrogen or a multi-phase synergy for absorption, making alloys achieve better hydrogen storage properties we need.

Non-stoichiometric alloys are selected to obtain higher storage capacities, lower plateau pressures, improved cycle life and easier activation [17]. The electrochemical properties are improved and hydride stability is reduced by a small substitution of Ti at Zr site in Zr-based AB_2 Laves alloys for Ni–MH rechargeable batteries [18]. The work of Kandavel et al. about hydrogenation properties of non-stoichiometric Zr-based AB_2 alloys gives the evidence that the hydrogenation kinetics and the amount of hydrogen absorption can be improved in over-stoichiometric alloys due to the increase in the atomic proportions of hydrogen absorbing elements, the plateau pressure increases for the contraction of unit cell volume [19–21]. From the above mentioned references summary, the structure usually does not change with the introduction of non-stoichiometry, but there is a small change in lattice parameters and considerable changes in their hydrogen storage properties such as plateau pressure, plateau slope and kinetics of sorption and electrochemical discharge capacity. It's evident that non-stoichiometry plays an important role on modification of hydrogen storage materials.

Up to now, the poor kinetics is still obstacle for application of Zr-based Laves phase alloys. The methods to improve hydrogenation kinetics in hydrogen storage alloys are basically non-stoichiometry, grain refinement and alloying, owing to the introduction of lattice distortion, micro-defects, larger specific surface area, the synergy of multi-phase structure and better affinity to hydrogen [12,14,21]. According to this, non-stoichiometry is a promising way to further improve hydrogenation kinetics on the base of

alloying. However, the mechanism about effect of non-stoichiometry on hydrogenation properties of pseudo-binary Zr–Ti–V Laves alloys is still uncertain. It is necessary to explore the interrelation between microstructure/phase constitute and hydrogenation kinetics/thermodynamic properties of non-stoichiometric Zr-based Laves alloys, which is beneficial for their practical application in fields of rapid storage and separation of hydrogen and its isotopes.

Considering all above, the $Zr_{0.9}Ti_{0.1}V_x$ alloys are designed where the Zr in A site is substituted by a small amount of Ti and the V in B site is non-stoichiometry based on our previous work about the role of defect structure on hydrogenation properties of $Zr_{0.9}Ti_{0.1}V_2$ [15]. In the present work, the effects of phase content, microstructure and cell volume on hydrogenation kinetics and thermodynamic properties of non-stoichiometric $Zr_{0.9}Ti_{0.1}V_x$ alloys are investigated. The defects in these alloys are observed, and the role of defects on hydrogenation kinetics is discussed. Detailed studies of hydrogenation kinetics are carried out to calculate reaction rate constant. Meanwhile, the mechanism about improvement of hydrogenation kinetics is further clarified. The possible hydrogenation mechanisms of non-stoichiometric $Zr_{0.9}Ti_{0.1}V_x$ alloys are proposed based on the aforementioned experiments. The hydrogen storage properties including PCT characteristic and thermodynamic parameters from 673 to 823 K are investigated.

2. Experimental procedures

Alloys with the compositions of $Zr_{0.9}Ti_{0.1}V_x$ ($x = 1.7, 1.8, 1.9, 2.1, 2.2, 2.3$) were prepared by non-consumable arc melting under argon atmosphere in a water-cooled copper crucible using 99.8wt% titanium, 99.4wt% zirconium and 99.5wt% vanadium. The ingots were turned over and re-melted 3 times to ensure the homogeneity, then annealed at 1273 K for 168 h in quartz tube under vacuum of 6×10^{-3} Pa followed by furnace cooling to room temperature. The phase compositions of the alloys were determined by a DX-2700 X-ray diffractometer using $Cu K_\alpha$ 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 and a transmission electron microscope (FEI Tecnai G2 F30, America) operating at 200 kV. The hydrogen storage characteristics including the P-t and PCT curves for each sample were obtained by using a Sievert type apparatus in temperature range of 673 K–823 K. The limits of the three capacitance manometers range from 100 kPa to 10^{-4} Pa. Prior to the absorption runs, each sample was activated by heating the sample chamber to 723 K and pumping the chamber for 40–60 min to the set vacuum in order to create a clean surface free from the effect of surface contamination. The hydrogen absorption content was determined by calculating the pressure variation during the reaction while maintaining constant temperature of the reaction chamber.

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