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Hydrogen absorption properties of $Zr(V_{1-x}Fe_x)_2$ intermetallic compounds

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ABSTRACT

The $Zr(V_{1-x}Fe_x)_2$ ($x = 0.02, 0.05, 0.10, 0.15, 0.25$) alloys were prepared by the arc-melt method and annealed at 1273 K for 168 h in an argon atmosphere. Phase structure investigations of the as-cast and annealed $Zr(V_{1-x}Fe_x)_2$ alloys indicate the annealing treatment can eliminate the minority phases originating from the non-equilibrium solidification of as-cast alloys. The ZrV_2 -type phase becomes the dominant one in each annealed alloy. The substitution of Fe in V sites leads to the contraction of their lattice. For annealed $Zr(V_{1-x}Fe_x)_2$ alloys, the P–t and PCT curves obtained between 673 K and 823 K give the evidence that the absorption process is controlled by a rate-controlling hydrogen diffusion. With the increase of iron, the equilibrium pressure and the plateau slope increase while the hydrogenation capacity and the absolute value of enthalpy and entropy decrease accordingly. The stability of metal hydride reduces gradually as the Fe content varies from $x = 0.02$ to 0.25 which promotes the hydrogen release and favors the practical applications of the $Zr(V_{1-x}Fe_x)_2$ alloys.

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1. Introduction

Hydrogen has attracted attention worldwide as an energy carrier and many believe it will be a vital component of clean renewable energy systems of the future [1]. How to store hydrogen is an important consideration for future hydrogen energy systems. Given their excellent hydrogen absorption ability and ease of activation, Zr-based intermetallic compounds with C14/C15-laves structure have potential application in the fields of hydrogen storage and separation and have been the subject of many studies over the past few decades [2–8]. The hydrogen absorption capacity of ZrV_2 can be as high as 4.8 H/M at 1 atm hydrogen partial pressure without any change in crystal structure [9]. However, ZrV_2 hydrides are too stable to release hydrogen easily which

makes it for ZrV_2 difficult to meet the requirements of rechargeable batteries and applications in the nuclear industry [9]. In addition, the high cost of vanadium and high pyrophoricity of ZrV_2 are also obstacles for practical applications.

To overcome these barriers, tremendous efforts have been devoted in past few decades to improving the hydrogen absorption properties of Zr-based Laves phase alloys. Boffito and coworkers have found that $ZrFe_2$ preserves the same structure with ZrV_2 but less reactive [10]. The partial substitution of vanadium by iron reduces the pyrophoricity and increases the stability of ZrV_2 . As a result, the stability of the hydrides can be reduced correspondingly according to “the rule of reversed stability” [2,11]. The crystal structure of $Zr(V_{1-x}Fe_x)_2$ changes as a function of the Fe content from

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a cubic MgCu_2 structure to the hexagonal MgZn_2 structure at around 17 at% iron [11]. Investigations on hydrogen absorption properties of $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ with a large amount substitution of vanadium by iron ($x \geq 0.25$) indicate the alloys exhibit excellent hydrogenation characteristics [11,12]. Particular attention has been focused on Zr-based alloys during past few decades for the potential applications in the field of bulk getters and rechargeable batteries. Although the hydrogenation performance of Zr-based intermetallic compounds preserves both theoretical and practical interests, there are few data about thermodynamic and kinetic properties in published literature. To achieve an insight into the hydriding mechanism is of great importance for hydrogen storage alloys since it always plays fundamental roles for further improvements of the hydrogenation performance. Unfortunately, the available data is still insufficient to understand the hydrogenation mechanism of $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ alloys. It is necessary to investigate the thermodynamic and kinetic properties of pseudo-binary $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ intermetallic compounds.

In this contribution, we chose the iron as the substitution element to prepare the $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ ($x = 0.02, 0.05, 0.10, 0.15, 0.25$) alloys. The phase composition, microstructure, absorption kinetics and thermodynamics of $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ were investigated. Meanwhile, the correlation between microstructure and hydrogenation properties of $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ was also evaluated. It is expected to explore a microstructural control method of Zr-based intermetallic compounds with the peritectic reaction during solidification. A possible influence mechanism of Fe on the microstructure and hydrogenation properties of pseudo-binary Zr ($\text{V}_{1-x}\text{Fe}_x$)₂ alloys is proposed.

2. Experimental procedure

Master alloys of $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ with $x = 0.02, 0.05, 0.10, 0.15, 0.25$ were prepared by the arc-melting method under an argon atmosphere using 99.9 wt% iron, at least 99.4 wt% zirconium and 99.5 wt% vanadium. During the melting process, the ingots were turned over and re-melted 3 times to ensure the homogeneity. All the ingots were homogeneously annealed at 1273 K for 168 h in an argon atmosphere. X-ray diffraction was used to investigate the phase structure of experimental alloys. With a continuous scanning mode ($2.0^\circ/\text{min}$), the diffraction data were collected at room temperature on a Rigaku D/MAX2500 diffractometer using $\text{Cu } K_\alpha$ radiation between 20° and 90° (2θ). The voltage and anode current were 40 kV and 250 mA, respectively. The microstructure of each sample was investigated by an Olympus GX51 optical microscope. The hydrogenation dynamic and thermodynamic properties were evaluated using a Sievert-type PCT equipment with ultra-high vacuum. The P–t and PCT curves were obtained between 673 K and 823 K by a continuous hydrogen charging technique at a constant temperature. The experimental sample was firstly loaded into the equipment at room temperature and pumped the chamber to the set vacuum. Then the hydrogen was charged into the chamber according to the required pressure. The amount of absorbed hydrogen was determined by the pressure variation during the reaction while maintaining constant temperature of the reaction chamber.

3. Results and discussion

3.1. Microstructure analysis

The XRD patterns of as-cast $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ ($x = 0.02, 0.05, 0.10, 0.15, 0.25$) alloys are shown in Fig. 1. In addition to the ZrV_2 -type dominant phase, the minority α -Zr, V enriched phase and $\text{Zr}_3\text{V}_3\text{O}$ phase are observed in as-cast alloys with $x = 0.02$ and 0.05 . Due to the non-equilibrium solidification process of the arc-melted ingots and the peritectic reaction during solidification in the pseudo-binary system, it is not strange to observe the minority phases and solidification segregation in the as-cast $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ alloys [13]. For the alloys with $x = 0.10$ and 0.15 , a small quantity of $\text{Zr}_3\text{V}_3\text{O}$ phase is detected in each alloy except for the major ZrV_2 -type one due to the residual oxygen in the melting chamber. No significant residual phases originating from the peritectic reaction are detected in $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ ($x = 0.10, 0.15$) alloys within the resolution of X-ray diffraction. With the further increase of the Fe content, several Bragg peaks of Zr_2Fe phase are identified in addition to the ZrV_2 -type dominant phase due to the possible peritectic reaction in $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ ($x = 0.25$) according to the Zr–V and Zr–Fe binary phase diagrams [13,14]. The effects of residual phases from the peritectic reaction and a small quantity of oxides on the hydrogen storage properties of AB_2 Zr-based intermetallic compounds are still controversial [15,16]. But the existence of the minority phases without hydrogen absorbing capacity inevitably decreases the volume fraction of the ZrV_2 -type phase for hydrogen storage. Accordingly, the hydrogen storage capability can be decreased due to the reduced quantity of the ZrV_2 -type effective absorbing phase. The single-phased samples are always pursued in the AB_2 Zr-based intermetallic compounds to improve the hydrogenation properties [17,18]. Therefore, it is necessary to eliminate these minority phases that originate from the peritectic reaction in the non-equilibrium solidification process of $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ alloys. XRD patterns of the annealed $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ alloys are displayed in Fig. 2(a). In the annealed state, the minority

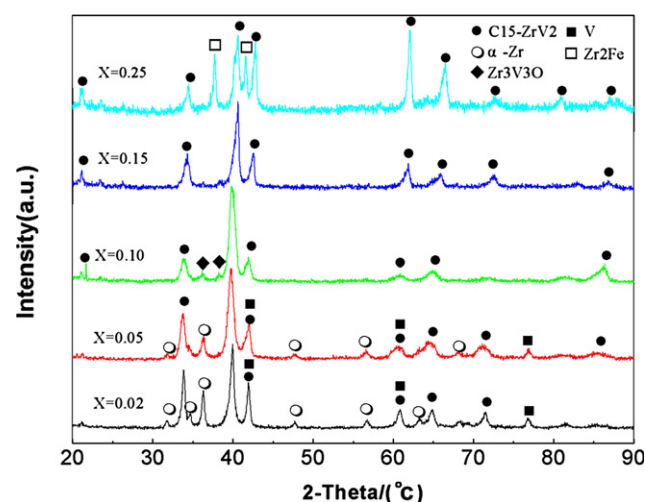


Fig. 1 – XRD patterns of as-cast $\text{Zr}(\text{V}_{1-x}\text{Fe}_x)_2$ ($x = 0.02, 0.05, 0.10, 0.15, 0.25$) alloys.

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