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Hydrogen storage properties and thermal stability of $V_{35}Ti_{20}Cr_{45}$ alloy by heat treatment

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ABSTRACT

The crystal structure, microstructure, hydrogen storage properties and thermal stability of the as-cast and annealed $V_{35}Ti_{20}Cr_{45}$ alloys prepared by arc-melting were studied in this work. It was confirmed that the as-cast alloy is a body-centered cubic (bcc) single phase, while it consists of bcc main phase and C14-typed Laves secondary phase after annealed at 973 K for 72 h. As a result of the microstructure change, the activation performance and kinetic properties of the annealed alloy are improved greatly due to the catalysis of C14-typed Laves secondary phase in the annealed alloy. The kinetic mechanism of hydrogen absorption/desorption processes in the as-cast and annealed alloys was discussed using the Johnson-Mehl-Avrami (JMA) equation. Based on the plateau pressure data from pressure-composition-temperature (PCT) measurements with the Van't Hoff equation, the calculated formation enthalpies of the hydride formed in the as-cast and annealed alloys indicate that heat treatment results in lower thermal stability of the hydride in the as-cast alloy. Furthermore, using the Kissinger method with the peak temperatures from differential scanning calorimeter (DSC) measurements at different heating rates, the calculated activation energies of the dehydrogenation in the as-cast and annealed alloys suggest that heat treatment is very beneficial to improve hydrogen absorption/desorption capacities in the alloy.

Introduction

Continuous search for suitable materials for the hydrogen storage system has been conducted because of further requirements of the dwindling fossil resources and growing environmental problems [1–7]. Among the developed hydrogen storage materials, V–Ti based hydrogen storage alloys are considered one of the promising candidates to effective hydrogen storage materials because of their large hydrogen absorption capacity compared with $AB_5/AB_2/AB$ typed hydrogen storage alloys as well as lower working temperature compared with Mg-based hydrogen storage alloys

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[8–12]. However, these alloys have some drawbacks such as difficult activation, poor kinetic characteristics and low hydrogen desorption capacity at room temperature [13–17]. In addition, the cost of the alloys with high content of V is very expensive due to its high price.

In the past decades, many researchers have strived to overcome the drawbacks mentioned above and improve hydrogen storage characteristics of V–Ti based alloys through the addition of alloying elements, heat treatment and different preparation methods (e.g. ball milling, rapid solidification) [18–22]. Especially, the addition of alloying elements with the transition metals (e.g. Cr, Fe, Mn, Ni, Zr, etc.) as an effective way has been widely used in the improvement of hydrogen storage properties in the V–Ti based alloys [18,19,23–25]. Among these alloying elements, Cr is the most effective one for enhancing the hydrogen desorption capacity and the cyclic ability [9,21,25]. On the other hand, it has been understood that heat treatment could influence significantly hydrogen storage properties of V–Ti based alloys (e.g. hydrogen desorption capacity and plateau pressure) [26–31]. In the study of hydrogen storage properties of $V_{35}Ti_xCr_y$ alloys annealed at 1173–1623 K for 1 min to 50 h, Okada et al. [26] found that the hydrogen desorption capacity of $V_{35}Ti_{25}Cr_{40}$ alloy annealed at 1573 K for 1 min is about 2.6 wt.% at 313 K. $V_{25}Ti_{32}Cr_{43}$ alloy with large hydrogen desorption capacity (2.3 wt.%) at 303 K after heat treatment (heated to 1653 K for 1 min at a rate of 20 K/min) was reported by Cho et al. [27]. Jeng et al. [28] studied $V_{33}Ti_{31}Cr_{21}Mn_{15}$ alloy, which has a flatter plateau pressure and a higher amount of desorption pressure after heat-treated at 1473 K for 10 h. However, the effect of heat treatment on hydrogen storage properties of Ti–V based alloys still needs to be investigated further to optimize heat treatment process including annealed temperature and time in order to improve activation performance, kinetic characteristics and hydrogen absorption/desorption capacities of V–Ti based alloys.

The purpose of the present work was to investigate the crystal structure, microstructure, thermal stability and hydrogen storage properties of $V_{35}Ti_{20}Cr_{45}$ alloy using X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), differential scanning calorimeter (DSC) and Sievert-type apparatus (Sateram PCTpro2000), respectively. The effect of heat treatment with lower temperature and longer time (973 K/72 h) on hydrogen storage properties and thermal stability of the alloy was thus discussed.

Experimental procedure

V (99.95% purity), Ti (99.95% purity), Cr (99.95% purity) were used as the starting materials. Ingots with nominal composition of $V_{35}Ti_{20}Cr_{45}$ alloy were prepared by arc-melting pure elements in an arc furnace using a non-consumable tungsten electrode under an inert argon atmosphere. Ingots were remelted four times in order to homogenize the alloy composition with a total mass loss of less than 1%. After annealed at 973 K for 72 h under vacuum atmosphere, ingots were quenched into ice-water.

The crystal structure and microstructure of alloy samples were examined by X-ray diffraction (XRD, Bruker D8 diffractometer, Cu K_α radiation) and scanning electron microscopy with energy dispersive spectrometry (SEM/EDS, Quanta450FEG/X-Max20). The hydrogen storage properties were measured using Sievert-type apparatus (Sateram PCTpro2000). For activation process, the powder (about 1 g) smashed from ingots was placed firstly in the reactor and evacuated for 15 min at 298 K, and then hydrogen was introduced gradually into the reactor up to a pressure of 2 MPa for the absorption process. Subsequently, the reactor was heated to 673 K and evacuated for 30 min for the next hydrogen absorption process. Hydrogen kinetic characteristics and pressure composition isothermal (PCT) measurements were carried out at 303 K, 333 K and 363 K, respectively. Thermal stability of the alloy was investigated using differential scanning calorimeter (DSC, Netzsch STA449 F3) under a flowing pure argon atmosphere at different heating rates of 5 K/min, 10 K/min, 20 K/min, 30 K/min, respectively. DSC measurements were calibrated using high pure In, Sn, Bi, Zn, Al as standard samples in order to eliminate the random errors and systematic errors, which provide an accuracy of ±0.5 K.

Results and discussion

Fig. 1 is XRD patterns of the as-cast and annealed $V_{35}Ti_{20}Cr_{45}$ alloys. As can be seen, the as-cast alloy is a single solid solution phase with body-centered cubic (bcc) structure, while it consists of a bcc main phase and a C14-typed Laves secondary phase after annealed at 973 K for 72 h. The intensity of diffraction peak of the bcc phase enhances after heat treatment, which implies that heat treatment promotes the crystallization of the bcc phase. However, the intensities of three peaks for the C14-typed Laves phase are weak because the phase fraction of this phase in the annealed alloy would be not too much. In addition, both the as-cast and annealed $V_{35}Ti_{20}Cr_{45}$ alloys were also examined by SEM/EDS as shown in Fig. 2. The SEM micrographs of the alloy show that the as-cast alloy is a single phase (the grey phase, 34.90 at.% V,

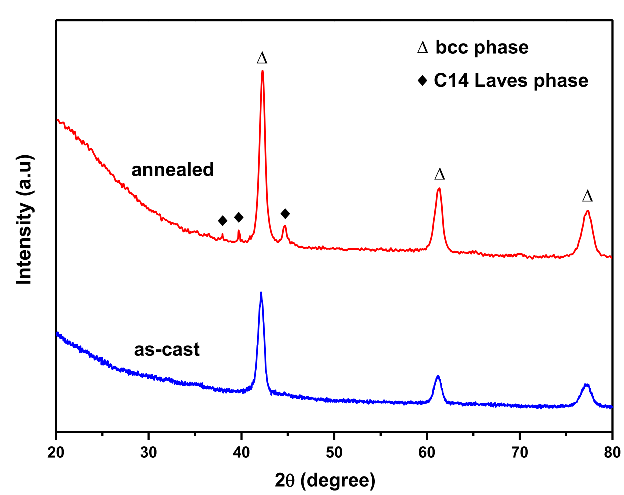

Fig. 1 – XRD patterns of the as-cast and annealed $V_{35}Ti_{20}Cr_{45}$ alloys.