Effect of Ti substitution on hydrogen storage properties of $Zr_{1-x}Ti_xCo$ ($x = 0$, 0.1, 0.2, 0.3) alloys

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Abstract

$Zr_{1-x}Ti_xCo$ ($x = 0$, 0.1, 0.2, 0.3) alloys were prepared by arc-melting method and the effect of Ti substitution on hydrogen storage properties was studied systematically. Hydrogen desorption pressure-composition-temperature (PCT) measurements were carried out using Sievert's type volumetric apparatus for ZrCo (at 473 K, 573 K and 673 K) and $Zr_{1-x}Ti_xCo$ alloys (at 673 K), respectively. Products after dehydrogenation were characterized by X-ray diffraction (XRD). In addition, the kinetics of $Zr_{1-x}Ti_xCo$ hydride was investigated at 473 K and 673 K, respectively, under hydrogen pressure of 5 MPa. Results showed that Ti substitution for Zr did not change the crystal structure of ZrCo phase. With the increase of temperature from 473 K to 673 K, the extent of disproportionation for ZrCo alloy increased. With Ti content increasing at 673 K, the desorption equilibrium pressure of $Zr_{1-x}Ti_xCo$-H_2 systems elevated and the disproportionation reaction of $Zr_{1-x}Ti_xCo$ alloys was inhibited effectively. Ti substitution decreased the kinetics rate and the effective hydrogen storage capacity of $Zr_{1-x}Ti_xCo$ alloys slightly. Generally speaking, it was found that $Zr_{0.8}Ti_{0.2}Co$ alloy had better anti-disproportionation property with less decrease of effective hydrogen storage capacity which was beneficial to tritium application in the International Thermonuclear Experimental Reactor (ITER).

Key words

ZrCo-based alloys; Ti substitution; hydrogen storage properties; anti-disproportionation

1. Introduction

As one of the major components of International Thermonuclear Experimental Reactor (ITER) fuel cycle, storage and delivery system (SDS) is mainly used to store hydrogen isotopes and deliver them to the fuel injection system [1–3]. U has been used in tritium handling application in SDS for many years, while the properties such as radioactivation, pyrophoricity, pulverization limited its further application. Compared with U, ZrCo possesses such properties as non-radioactivation, low pyrophoricity, low equilibrium absorption pressure at room temperature, high hydrogen storage capacity, and the ability of trapping ³He that released when tritium decays [4], which is attractive for tritium handling instead of U in facilities like SDS. Penzhorn et al. [5] presented that ZrCo alloy might replace U for interim storage of tritium in technical applications because of its advantages over U. The study by Bekris et al. [6] confirmed that ZrCo alloy

was adequate for the storage of tritium and other hydrogen isotopes within the Tritium Plant of ITER. Hayashi et al. [7] had mentioned that during the long-term storage, it is effective for ZrCo to monitor and control of ³He released from tritide.

However, investigations showed that once ZrCo alloy is disproportionate in hydrogen isotopes handling, it loses its ability to absorb and desorb hydrogen isotopes reversibly. Besserer et al. [8] measured the disproportionation rate in the temperature range of 573 K to 743 K under equilibrium hydrogen pressures and they observed the disproportionation above 573 K. Hara et al. [9] presented that the hydrogen-induced disproportionation is an intrinsic nature of ZrCo alloy during its hydrogen absorption and desorption process. The study by Devillers et al. [10] revealed that the disproportionation reaction of ZrCo with H_2 follows the next equation:

$$2ZrCoH_x \longrightarrow ZrH_2 + ZrCo_2 + (x-1)H_2 \qquad (1)$$

It can be seen that the disproportionation of ZrCo alloy

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results in the formation of $ZrCo_2$ phase and ZrH_2 hydride phase. Since the decomposition of ZrH_2 requires much higher temperature (>973 K) than that of ZrCo hydride and $ZrCo_2$ is usually not active for absorption of hydrogen isotopes, a significant amount of hydrogen gets trapped within the storage material. This results in the reduction of hydrogen storage capacity of ZrCo significantly, which is not desirable for its use in SDS. Therefore, it is necessary to improve the ability to inhibit the disproportionation of ZrCo alloys.

Element substitution is considered to be an effective way to improve the hydrogen storage properties of ZrCo-based alloys, which has been investigated by many researchers [11−14]. The study by Tan et al. [11] revealed that substitution of Hf for Zr obviously elevates the equilibrium dehydrogenation pressure of ZrCo alloy with enough high hydrogen storage capacity at room temperature. The hydrogen absorption-desorption cyclic life study at 583 K by Jat et al. [12] reported that the cyclic stability of $ZrCo_{1-x}Ni_x$-H_2 ($x = 0, 0.1, 0.1, 0.3$) systems improved with the increase of Ni content, whereas all the compositions of alloys showed disproportionation behavior with the formation of ZrH_2 and $ZrCo_2$ phases. Peng et al. [13] confirmed that $Zr_{0.7}Hf_{0.3}Co$ has much better ability of anti-disproportionation than ZrCo when the temperature was increased from 673 K to 823 K. Nevertheless, the cost of Hf is too high for application.

Ti is often used as an additive for Zr-based alloys, since Zr and Ti are in the same main family, and ZrCo and TiCo have the same structure of CsCl. Meanwhile, Ti has good hydrogen absorption kinetics properties so as to form a solid solution with Zr easily [15] and TiH_2 is not stable as ZrH_2 thermodynamically [16], so Ti substitution in ZrCo alloy is expected to partly inhibit the hydrogen-induced disproportionation. $Zr_{1-x}Ti_xCo$ ($x = 0, 0.1, 0.2, 0.3$) alloys were synthesized by Huang et al. [17], and it was found that the desorption temperatures of the alloys for supplying 100 kPa hydrogen decrease with the increasing Ti content. But investigations of hydrogen storage properties especially the anti-disproportionation of $Zr_{1-x}Ti_xCo$ alloys above 633 K has not been reported which is very important for the application of ZrCo alloys in SDS.

In this paper, the effect of Ti substitution on hydrogen storage properties including the ability of ant-disproportionation of $Zr_{1-x}Ti_xCo$ ($x = 0, 0.1, 0.2, 0.3$) alloys at 673 K has been described in detail.

2. Experimental

2.1. Material preparation and characterization

$Zr_{1-x}Ti_xCo$ ($x = 0, 0.1, 0.2$ and 0.3) alloys were prepared by arc-melting method under argon atmosphere in a water cooled copper crucible. Stoichiometric amounts of high purity ($\geqslant 99.5\%$) Zr, Co and Ti metals were melted four times in order to ensure compositional homogeneity.

The ingots were crumbled mechanically into powder of 400 mesh and then characterized by X-ray diffraction (XRD), which was carried out using Rigaku D/max-2500. The XRD patterns were recorded using Cu K_α radiation, 40 kV and 200 mA, with $K_\alpha 1$ graphite monochromator. Phase identification of alloys was confirmed by comparing their XRD patterns with the Joint Committee on Powder Diffraction Standards (JCPDS) files [18]. Furthermore, the lattice parameters and phase abundances of the alloys were calculated by Jade 5.0 software.

2.2. Pressure-composition-temperature measurements

The pressure-composition-temperature (PCT) measurements were carried out using a conventional Sievert's type volumetric apparatus (PCT Pro-2000, SETARAM). A known amount of fully activated ZrCo alloy was loaded into the reaction vessel of known volume and thereafter, hydrogen gas (purity 99.999%) at a known pressure was introduced at 473 K. The system was allowed to attain equilibrium by monitoring the pressure change with time. The hydrogen concentration in the specimen was calculated from the pressure data. This hydride phase was then decomposed at the same temperature to generate desorption PCT curves. Desorption equilibrium was established by evacuating a known amount of hydrogen from the reservoir and allowing the system to reattain equilibrium. This allows to calculate the value of hydrogen concentration (i.e. n_H/n_{ZrCo}) and the corresponding equilibrium hydrogen desorption pressure at the experimental temperature simultaneously. Thereafter, the value of n_H/n_{ZrCo} was altered by aliquoting a known amount of hydrogen from the reservoir and allowing the attainment of a new equilibrium.

This process was repeated till the entire isotherm was generated. Following this procedure, PCT curves of absorption and desorption for $ZrCo-H_2$ systems were generated at 573 K and 673 K, respectively. Thereafter, the PCT curves of absorption and desorption for $Zr_{1-x}Ti_xCo-H_2$ systems were generated at 673 K using the same procedure as $ZrCo-H_2$, while they were kept homeothermic for 6 h at 673 K before dehydrogenating to obtain the disproportionation rate quantitatively.

2.3. Hydrogen-induced disproportionation studies

The process to investigate the rate of hydrogen-induced disproportionation was described as follows. Firstly, the ZrCo-based alloys absorbed hydrogen to saturation at different temperatures, and then decomposed at the corresponding temperature as described in Section 2.2. It is known that the hydrogen-induced disproportionation results in the formation of a hydrogen non-absorbing $ZrCo_2$ phase and a very stable ZrH_2 hydride phase [10]. Therefore, the systems