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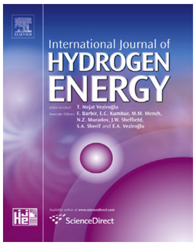

Structural and hydrogen isotope storage properties of Zr–Co–Fe alloy

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ABSTRACT

In the present study, the effect of Fe substitution for Co on the hydrogen isotope storage properties of ZrCo alloy has been investigated to ascertain the improvement in durability of ZrCo alloy against hydrogen induced disproportionation. The $ZrCo_{0.9}Fe_{0.1}$ alloy was synthesized by arc melting and characterized by X-ray diffraction analysis, SEM and EDS. Hydrogen isotope storage behavior of this alloy was probed by generating the hydrogen/deuterium desorption pressure–composition isotherms (PCIs) for $ZrCo_{0.9}Fe_{0.1}$–H_2/D_2 systems. Thermodynamic parameters like enthalpy and entropy change for desorption of hydrogen/deuterium in the $ZrCo_{0.9}Fe_{0.1}$–H_2/D_2 systems were derived from the van't Hoff plots. This study reveals the normal hydrogen isotope effect for this alloy, depicting the higher equilibrium pressure of D_2 than that of H_2 at all experimental temperatures. In addition, the cyclic life studies were also performed on $ZrCo_{0.9}Fe_{0.1}$ alloy at 583 K up to 50 cycles of hydrogen/deuterium absorption–desorption. Neutron diffraction studies were also carried out on $ZrCo_{0.9}Fe_{0.1}$ deuteride to determine its crystal structure and interstitial sites occupied by deuterium atoms. The experimental results show that Fe substitution increases the durability against hydrogen induced disproportionation as compared to pure ZrCo alloy, which makes it favorable for storage of hydrogen isotopes.

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Introduction

The intermetallic compound ZrCo is being considered as an appropriate candidate material for storage, supply and recovery of hydrogen isotopes in International Thermonuclear Experimental Reactor (ITER) [1–5]. The competitiveness of ZrCo with uranium is mainly due to its non-radioactive nature, non-pyrophoricity at room temperature [6] and tritium storage properties similar to uranium [7]. Apart from the high storage capacity of ZrCo (H/ZrCo up to 3) [2], it has the drawback of hydrogen induced disproportionation upon repeated hydrogen absorption–desorption cycles [8]. The hydrogen induced disproportionation reaction can be written as:

$$2ZrCoH_x \rightarrow ZrH_2 + ZrCo_2 + (x-1)H_2 \quad (1)$$

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The reaction product ZrH_2 is a highly stable compound and requires higher temperature (>973 K) to desorb the absorbed hydrogen gas. The other reaction product $ZrCo_2$ is a hydrogen non-absorbing compound. Subsequently, the storage capacity of ZrCo decreases upon repeated hydriding–dehydriding cycles and also a significant amount of hydrogen gets trapped within the storage material. This type of disproportionation nature of ZrCo is not favorable for its use in ITER Storage and Delivery System (SDS). Several attempts have been made to improve the durability of ZrCo against disproportionation by substituting either Zr or Co with a third element without substantially altering the storage properties. A number of studies have been reported in the literature on the effect of ternary alloying on the hydrogen storage behavior of ZrCo based alloys [5,9–13]. In an earlier study, Jat et al. [5] have thoroughly investigated the effect of Ni content on the hydrogen storage behavior of $ZrCo_{1-x}Ni_x$ alloys and reported that Ni substitution improves the durability of ZrCo against disproportionation.

Tritium being a radioactive gas, many of the experiments related to development of tritium storage materials are usually carried out using hydrogen and deuterium. Owing to the similar chemical properties, reactions of hydrogen, deuterium and tritium gases with metals/alloys form their corresponding hydrides, deuterides and tritides with same stoichiometry. However, the lattice dynamics of the hydrides, deuterides and tritides differ considerably due to the difference in their zero point vibrational energies. Additionally, the difference in molecular masses of hydrogen, deuterium and tritium results in different values of their standard entropies. The overall effect of difference in zero point energies and the standard entropies lead to different values of Gibbs free energy of formation for these analogous compounds, which in turn, gives different values of equilibrium pressures for H_2, D_2 and T_2 at a particular temperature [14]. Hence, it is important to investigate the hydrogen isotope effect on the storage behavior of these metals and alloys.

The present study is aimed at investigating the effect of Fe substitution on the hydrogen isotope storage behavior of ZrCo alloy. The phase diagram of Co–Fe system suggests that Fe has very limited solubility (~10 atom% at 773 K) in Co [15]. Therefore, in the present work it was decided to investigate the hydrogen isotope storage behavior of $ZrCo_{0.9}Fe_{0.1}$ alloy by generating the hydrogen/deuterium desorption pressure–composition isotherms (PCIs) and studying the hydrogen/deuterium absorption–desorption cycles. Structural studies were also carried out on $ZrCo_{0.9}Fe_{0.1}$ deuteride by employing the neutron powder diffraction (NPD) technique to understand the effect of Fe substitution on deuterium site occupancy. The work presented here is useful in predicting the nature of hydrogen isotope effect which can be used to predict the tritium equilibrium pressure of the alloy for its use in ITER SDS.

Experimental

Materials preparation and characterization

$ZrCo_{0.9}Fe_{0.1}$ alloy was synthesized by arc-melting of stoichiometric amounts of high purity zirconium (purity 99.98%), cobalt (purity 99.95%) and iron (purity 99.99+%) metals in a water cooled copper hearth, under helium atmosphere. In order to improve the homogeneity, the cast ingot was turned around and re-melted six times. The annealing of the ingot was carried out at 973 K for 72 h in an evacuated sealed quartz ampoule. To getter the residual oxygen present in sealed quartz ampoule the ingot was wrapped in tantalum foil. After annealing, the ampoule was subjected to water quenching to room temperature. The formation of alloy was confirmed by X-ray powder diffraction method.

For the preparation of the $ZrCo_{0.9}Fe_{0.1}$ hydride/deuteride, the alloy sample was initially activated by hydriding–dehydriding method described in an earlier publication [5]. The activated alloy was therefore loaded in the reaction vessel kept at room temperature and allowed to react with a known amount of hydrogen/deuterium gas to form the hydride/deuteride phase. X-ray powder diffraction method was used to characterize the synthesized hydride/deuteride phases.

The X-ray powder diffraction patterns were recorded using CuK_α radiation in a theta–theta geometry diffractometer (supplied by GNR Analytical Instruments Group, Italy; Model: EXPLORER) equipped with a graphite monochromator positioned in the diffracted beam.

The microstructure and surface morphology of $ZrCo_{0.9}Fe_{0.1}$ alloy and its hydride phase were analyzed by Scanning Electron Microscope (SEM, SERON INC South Korea, Model ATS 2100). The EDX spectroscopy and elemental mapping were used for compositional analysis and to investigate the homogeneity of the alloy.

Pressure–composition–temperature measurements

A conventional Sievert's type volumetric apparatus (PCT Pro-2000, SETARAM Instrumentation, France) was used for the generation of pressure–composition isotherms (PCIs). The details of PCI generation method have been described in an earlier publication [5]. The desorption pressure–composition isotherm at a desired temperature was generated by using a hydride phase in a known volume reaction vessel of the Sievert's apparatus with known over pressure of hydrogen in the system. At every point of isotherm the system was allowed to attain equilibrium which was monitored by change in pressure with time. The attainment of equilibrium was considered only when there was no discernible change in pressure reading for a period of 3–4 h. The hydrogen concentration in the specimen was calculated using the data for temperature, pressure and volume. Thus the value of hydrogen concentration (=H/f.u., f.u. = $ZrCo_{0.9}Fe_{0.1}$) and the corresponding equilibrium hydrogen desorption pressure at the experimental temperature were obtained simultaneously. Subsequently, for the next point of desorption isotherm a known amount of hydrogen was removed from the reservoir and the system was allowed to re-attain the equilibrium. The complete desorption isotherm was generated by repeating the prior steps of aliquoting the gas from reservoir and attainment of new equilibrium. Similar method was used for generation of PCIs for $ZrCo_{0.9}Fe_{0.1}$ –H_2/D_2 systems in the temperature range of 523–583 K with an increasing interval of 20 K.

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