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Comparative study of full-scale thin double-layered annulus beds loaded with ZrCo, $Zr_{0.8}Hf_{0.2}Co$ and $Zr_{0.8}Ti_{0.2}Co$ for recovery and delivery of hydrogen isotopes

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ABSTRACT

Metal hydride bed is a necessary component for deuterium–tritium fusion energy under development in International Thermonuclear Experimental Reactor (ITER), which is used for rapid and safe recovery/delivery of hydrogen isotopes. In the present work, full-scale thin double-layered annulus beds loaded with ZrCo, $Zr_{0.8}Hf_{0.2}Co$ and $Zr_{0.8}Ti_{0.2}Co$ were fabricated. The corresponding hydrogen storage behaviors including hydrogen recovery/delivery and cycling properties of the three beds were systematically investigated and compared. It was found that all the three fabricated beds could reach the hydrogen storage target of 17.5 mol. Compared with ZrCo bed and $Zr_{0.8}Hf_{0.2}Co$ bed, $Zr_{0.8}Ti_{0.2}Co$ bed exhibited superior hydrogen delivery properties in terms of higher hydrogen delivery amount, faster delivery rate and better cyclic delivery performance, which could deliver 17.06 mol H_2 (~94.7% of total capacity) at 450 °C within 31.8 min holding at the critical delivery rate of 20 Pa m^3/s. Although the hydrogen delivery amount gradually decreased during the recovery/delivery cycles, which was revealed to be caused by the characteristic disproportionation of ZrCo based alloy, significant improvement had been gained for $Zr_{0.8}Ti_{0.2}Co$ bed relative to ZrCo bed and $Zr_{0.8}Hf_{0.2}Co$ bed. In addition, the industrial computed tomography (ICT) results showed that the thin double-layered annulus bed owned good structural stability during the hydrogen recovery/delivery cycles. In view of its beneficial hydrogen recovery and delivery performances, the $Zr_{0.8}Ti_{0.2}Co$ bed with thin double-layered annulus configuration appeared to be a potential option for hydrogen isotopes recovery and delivery in ITER if the anti-disproportionation property could be further enhanced.

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Introduction

The falling accessibility of natural resources, rising consumption of energy and growing environmental pollution have nagged many countries throughout the world. Developing a reliable, clean and renewable energy has gained particular attention in recent decades. Hydrogen and its isotopes as perfect fuel and clean energy carriers have drawn great attention worldwide. Hydrogen energy may serve as an alternative energy source for transportation application due to its high calorific value and environmental friendliness, which converts hydrogen to power by fuel cells or hydrogen combustion engines with the only byproduct being water [1–3]. Meanwhile, fusion energy based on the hydrogen isotopes is also considered as the main energy source for human in the future because of its high energy density, abundant source of fuel and environmental benignity [4]. The International Thermonuclear Experimental Reactor (ITER), which generates power by burning plasma of deuterium and tritium, is the most famous fusion reactor being developed by its project members of one organization and six countries, including the E.U., the United States, Russia, China, Japan, South Korea and India. As fuel for ITER, the deuterium–-tritium gases should be safely and efficiently recovered and stored since tritium is radioactive and rare, though deuterium is stable and abundant. At the same time, the deuterium–-tritium gases are required to be supplied rapidly to the fueling system in ITER [5]. Therefore, it is very crucial to develop a safe and rapid hydrogen isotopes recovery, storage and delivery technology for deuterium–tritium fusion energy.

Since deuterium and tritium are the isotopes of hydrogen, the hydrogen storage technologies are usually applied to hydrogen isotopes recovery and delivery [6]. Solid-state hydrogen storage, utilizing metal hydrides to recover/deliver hydrogen under moderate temperature and pressure, offers safety and cost advantages over the gas and liquid storage methods [7,8]. In addition, metal hydrides have higher storage capacity by volume than hydrogen gas or liquid hydrogen [9]. Depleted uranium (DU) and an intermetallic compound of ZrCo are considered as suitable solid materials to be used for hydrogen isotopes processing, especially for tritium storage, due to their low equilibrium dissociation pressure, fast kinetics of hydrogen recovery and material stability for the storage tritium [10,11]. However, the drawbacks of DU, such as radioactivation, pyrophoricity, pulverization, result in a limitation on its further application [12]. Meanwhile, our recent study showed that the remarkable volume expansion of DU during the hydrogen recovery and delivery cycles would lead to obvious deformation of the filters in the metal hydride bed [13]. Compared with DU, ZrCo possesses such advantageous properties as non-radioactivation, low pyrophoricity, high hydrogen storage capacity [14–17]. Moreover, the feature of ZrCo that the temperature at which its equilibrium pressure reaches 1 bar is not too high is beneficial to minimizing tritium permeation loss in metal hydride bed during the delivery process [18]. In view of these, ZrCo has received considerable attention from the ITER team as an important candidate material for the recovery, storage and delivery of deuterium–-tritium gases [19].

Nevertheless, the disproportionation of ZrCo, which will result in significant degradation of hydrogen storage properties, throws a big obstacle on the way of its wide application [20]. It has been reported that the disproportionation of ZrCo is easily induced during the hydrogen recovery/delivery processes following the reaction [21]:

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

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 recovery of hydrogen isotopes, a noticeable amount of hydrogen gets trapped in the products of disproportionation reaction [22]. As a result, ZrCo will lose its hydrogen isotopes storage ability when disproportionation reaction occurs. Therefore, it is necessary to minimize or address the disproportionation problem of ZrCo.

It seems that element substitution is an effective method for solving this problem, which has been investigated by many researchers. Tan et al. [23,24] reported that the equilibrium dehydrogenation pressure of $Zr_{1-x}Hf_xCo$ alloy increases obviously with increasing Hf content, which is favorable to improve the ability to inhibit the disproportionation of ZrCo. Peng et al. [25] confirmed that the disproportionation rate and disproportionation extent of ZrCo decrease with Hf substitution ratio increasing. Huang et al. [26] studied the hydrogen storage properties of $Zr_{1-x}Ti_xCo$ intermetallic compound. It was found that the equilibrium hydrogen desorption pressure of $Zr_{1-x}Ti_xCo$ alloy increases along with increasing Ti content and repeated hydrogen absorption and desorption cycles do not generate separated ZrCo, TiCo and ZrH_2, indicating that Ti substitution is useful for improving the anti-disproportionation property of ZrCo alloy. Zhao et al. [27] systematically investigated the effect of Ti substitution on hydrogen storage properties of $Zr_{1-x}Ti_xCo$ alloys. They discovered that $Zr_{0.8}Ti_{0.2}Co$ alloy has better anti-disproportionation property which is quite advantageous to tritium handling in ITER. Recently, Zhang et al. [28] conducted a comparative study of Ti, Ni, Sc, Fe substitution on the thermal stability of ZrCo alloy. It was shown that desorption plateau pressure increases in order of $ZrCo_{0.8}Fe_{0.2}$ < ZrCo < $Zr_{0.8}Sc_{0.2}Co$ < $ZrCo_{0.8}Ni_{0.2}$ < $Zr_{0.8}Ti_{0.2}Co$ and $Zr_{0.8}Ti_{0.2}Co$ exhibits the most prominent property of anti-disproportionation. Tan et al. [24] also showed that substitution of Sc for Zr slightly enhances the anti-disproportionation property of ZrCo alloy but makes its dehydrogenation more difficult. Jat et al. [29–31] observed that the durability against disproportionation of $ZrCo_{1-x}Ni_x$ alloys increases with increasing Ni content. Unfortunately, all the compositions of alloys in their study still show disproportionation behavior with formation of ZrH_2 and $ZrCo_2$ phases upon cycling. In addition, Jat et al. investigated the effect of Fe substitution for Co on the hydrogen storage properties of ZrCo alloy [32]. It was found that improvement in durability of ZrCo alloy against hydrogen induced disproportionation could be obtained by $ZrCo_{0.9}Fe_{0.1}$. However, significant decrease in hydrogen storage capacity was also observed after hydrogen absorption and desorption cycles. Previous studies suggested that element substitution indeed has significant effects on the hydrogen storage performances, especially anti-disproportionation