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Effect of Ni substitution on hydrogen storage properties of $Zr_{0.8}Ti_{0.2}Co_{1-x}Ni_x$ ($x = 0, 0.1, 0.2, 0.3$) alloys

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ABSTRACT

$Zr_{0.8}Ti_{0.2}Co_{1-x}Ni_x$ ($x = 0, 0.1, 0.2, 0.3$) alloys were prepared by vacuum arc-melting method. The microstructure and hydrogen storage properties including cyclic stability, disproportionation rate and hydriding kinetics of the alloys at 573 K and 673 K were studied respectively. X-ray diffraction (XRD) analyses show that all original alloys consist of single ZrCo phase. At 573 K, with Ni content increasing, the hydrogen storage capacity retention of the alloys increases from 58.7% ($x = 0$) to 76.3% ($x = 0.3$) obviously after 15 hydriding/dehydriding cycles which can be mainly attributed to the enhancement of anti-pulverization capability for the alloys after Ni partial substitution for Co. However, at 673 K, hydrogen-induced disproportionation becomes the main factor for the deterioration of hydrogen storage properties for the alloys. Kinetics test shows that the hydriding speed of the alloys at 573 K increases gradually with Ni content increasing since Ni acts as a catalyst during hydrogen absorption process. In addition, the hydrogen desorption curves at 673 K reveal that Ni partial substitution for Co deteriorates the anti-disproportionation property of the alloys slightly.

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Introduction

Owing to the sharp depletion of fossil fuels and the growing environmental pollution, there is an urgent need to develop clean and renewable energy [1–5]. Fusion energy under development in International Thermonuclear Experimental Reactor (ITER), which burns equimolar deuterium–tritium mixtures, is considered as the main energy source for human

in the future because of its high energy density, abundant source of fuel and environmental benignity [6–9]. In ITER, the fuel storage and delivery system (SDS) is designed to store and deliver tritium from tritium source to Tokamak vessel for participating the subsequent reaction [10]. Consequently, sustained, safe and efficient delivery for tritium is particularly important which can insure the thermonuclear fusion reaction is carried out smoothly and there is an urgent need to find appropriate materials for storage, delivery and supply of

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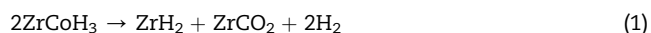
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hydrogen isotopes in SDS of ITER. Due to favorable hydrogen storage properties, Uranium (U) has been used to charge/discharge tritium for many years [11,12]. However, it is well known that U is one kind of radioactive material and can be pyrophoric easily at room temperature, both of which restrict its further application. Therefore, investigation on searching a candidate material for hydrogen isotopes storage is in process. ZrCo intermetallic compound has gained great attention due to the high hydrogen absorption capacity, the trapping ^3He ability, especially the low equilibrium pressure and non-radioactive nature which can significantly improve the safety during the hydrogen isotopes storage and delivery [13,14]. Therefore, ZrCo alloy is an alternative material to replace U and possesses prospective applications in ITER.

However, there are still some drawbacks such as hydrogen-induced disproportionation, stagnant hydriding/dehydriding cyclic stability and poor kinetics properties which block the adhibition of ZrCo alloy in practice. The hydrogen-induced disproportionation is due to the intrinsic nature of this kind of alloy namely formation of a thermodynamically more stable hydride through hydrogen absorption by the alloy, and subsequent decomposition of the alloy to form a stable hydride and a new metallic compound deficient in the hydride forming element [15]. Devillers et al. [16] observed disproportionation phenomenon of ZrCo alloy in the temperature rang of 623–773 K and the relative reaction follows the next equation:



The disproportionation reaction deteriorates the hydrogen storage performance of ZrCo alloy obviously owing to stable thermodynamic property of ZrH_2 and the very limited hydrogen storage capability of ZrCo_2 . Jat et al. [17] investigated the cyclic stability of ZrCo alloy at 573 K and found that with cycle number increasing, the hydrogen capacity decreased substantially. It is worthy noted that the working temperature is usually selected in the range 573 K–673 K to avoid disproportionation reaction and to ensure a completely desorption. Meanwhile, it was reported that the delivery rate of ZrCo bed was still unable to meet the requirement of fast hydrogen delivery for the practical application [18]. The alloys with poor cycle life and sluggish kinetic property will reduce efficiency for the storage and delivery which will go against the smooth supply of tritium fuel in ITER system.

Many efforts have been made to improve the ability of anti-disproportionation for ZrCo-based alloys. Peng et al. [19] doped Hf to partially substitute Zr in ZrCo alloy and found that $\text{Zr}_{0.7}\text{Hf}_{0.3}\text{Co}$ alloy had much better ability of anti-disproportionation than the original alloy in hydrogen pressure of about 200 kPa when temperature increased from 673 K to 828 K. Jat et al. [20] investigated the effect of Fe substitution for Co to ascertain the improvement in durability of ZrCo alloy against hydrogen-induced disproportionation.

According to the previous studies about ZrCo-based alloys [21,22], the deterioration of hydrogen storage capacity was mainly attributed to hydrogen-induced disproportionation while the pulverization of the alloy particles has rarely been

considered. In fact, alloy pulverization is an important factor for the deterioration of hydriding/dehydriding cyclic stability which has been proved in many other kinds of hydrogen storage alloys. Lin et al. [23] observed the degradation of hydrogen storage capacity of TiCrV and $\text{Ti}_{0.8}\text{Cr}_{1.2}\text{V}$ alloys during hydriding/dehydriding cycles and discovered pulverization of the alloys after 15 cycles. Li et al. [24,25] investigated the cyclic life of La–Mg–Ni-based hydrogen storage alloy electrodes and pointed out the alloy pulverization was one of the important factors which deteriorated the hydrogen storage capacity of the alloys. Thus, it is very important to conduct the study on ZrCo-based alloys with a good cycle life which means possessing better anti-disproportionation and anti-pulverization ability for ensuring the smooth supply of the tritium fuel in ITER system.

For hydrogen storage alloys, Ni is usually used as a substitution element to improve overall hydrogen storage performance. Lv et al. [26] investigated the effect of Ni content on hydrogen storage properties of Mg–xNi–3La ($x = 5\text{--}20$ at.%) alloys and found that all the alloys show excellent desorption kinetics. Moreover, it has been found that Ni substitution for Co can improve the cyclic stability of ZrCo alloy at 573 K [17]. In our earlier study [27], we found that compared with the original ZrCo alloy, $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{Co}$ alloy had better anti-disproportionation property with less decrease of effective hydrogen storage capacity. In order to improve the overall hydrogen storage properties of ZrCo-based alloys further, in this work, we designed the alloys with chemical composition of $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{Co}_{1-x}\text{Ni}_x$ ($x = 0, 0.1, 0.2, 0.3$) and investigated the effect of Ni substitution on hydrogen storage performance including hydrogen absorption/desorption behavior, cyclic stability, disproportionation rate and hydriding kinetics of the alloys.

Experimental

$\text{Zr}_{0.8}\text{Ti}_{0.2}\text{Co}_{1-x}\text{Ni}_x$ ($x = 0, 0.1, 0.2, 0.3$) alloys were prepared by vacuum arc-melting under 0.02 MPa argon atmosphere. The raw materials were purchased from Hongyan, Co. Ltd. and the purity of raw materials Zr, Ti, Co and Ni was all above 99.9%. The ingots were re-melted three times by turning the ingots upside down to insure the homogeneity.

The hydrogen storage properties of the alloys were measured using an automatically controlled Sievert-type apparatus (PCT-1SPWIN, Suzuki). The samples were crushed into particles of $-10 \sim +20$ mesh size by mortar and pestle and about 1 g such particles were used for characterization of the hydrogen storage properties. The activation process of samples was conducted in an airtight container as following: after evacuation at 473 K for 30 min, the samples absorbed hydrogen under an initial hydrogen pressure of 5 MPa in the container for 30 min and then were heated to 573 K to desorb hydrogen for 50 min under dynamic vacuum to make the samples activated. For pressure-composition isotherms (P–C–T) curves test, the completely activated samples absorbed hydrogen to saturation at 473 K with an hydrogen pressure in the channel of 5 MPa and then were heated to 673 K to desorb hydrogen. The initial pressure for desorption is controlled at 5 MPa. Desorption equilibrium was established

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