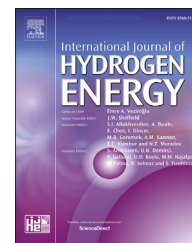




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Temperature-hydrogen pressure phase boundaries and corresponding thermodynamics for ZrCo–H system

Huaqin Kou^{a,c,*}, Wenhua Luo^b, Tao Tang^a, Zhiyong Huang^a,
Ge Sang^{a,**}, Huan Wang^a, Changan Chen^a, Guanghui Zhang^a,
Jinchun Bao^a, Yan Xue^a

^a Institute of Materials, China Academy of Engineering Physics, P. O. Box 9071-12, Mianyang 621907, China

^b Science and Technology on Surface Physics and Chemistry Laboratory, P. O. Box 9072-35, Mianyang 621908, China

^c State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

The thermodynamically and kinetically stable regions of the temperature–H₂ pressure phase boundaries for the ZrCo–H system were established using the Temperature-Concentration-Isobar (TCI) method. Based on this, the enthalpy change and entropy change values of dehydrogenation and disproportionation reactions were successfully obtained. The average enthalpy change (ΔH) and entropy change (ΔS) estimated from the phase boundaries for dehydrogenation of ZrCoH₃ to ZrCo are respectively 103.07 kJ mol⁻¹H₂ and 148.85 J mol⁻¹ H₂ K⁻¹, which are well agreement with the data reported in literature. The average ΔH and ΔS were estimated to be -120.91 kJ mol⁻¹H₂ and -149.32 J mol⁻¹ H₂ K⁻¹ for the disproportionation of ZrCoH₃, whereas the ΔH and ΔS were calculated to be -84.6 kJ mol⁻¹H₂ and -92.29 J mol⁻¹ H₂ K⁻¹ for disproportionation of ZrCo. In addition, it was found from the established phase boundaries that the anti-disproportionation property of ZrCo alloy can be enhanced if the phase boundaries of hydrogenation/dehydrogenation are far away from the phase boundaries of disproportionation by adjusting the thermodynamics. Meanwhile, it is possible to keep ZrCo away from disproportionation even at high temperature of 650 °C under hydrogen atmosphere, if the temperature-H₂ pressure trajectory is carefully controlled without crossing the phase boundaries of disproportionation. Therefore, the established phase boundaries can be used as a guide to the eye avoiding disproportionation and improving the anti-disproportionation property of ZrCo alloy.

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Introduction

Serious concerns about energy security, climate change, resource sustainability and human health have led to continued efforts to develop sustainable and clean sources [1].

Recently, fusion energy under development of the International Thermonuclear Experimental Reactor (ITER), which releases tremendous power by burning plasma of deuterium and tritium, has attracted considerable attention as an ideal energy source because of its high energy density, abundant source of fuel and environmental benignity [2–4]. As fuel for

* Corresponding author. Institute of Materials, China Academy of Engineering Physics, P. O. Box 9071-12, Mianyang 621907, China.

** Corresponding author.

E-mail addresses: kouhuaqin@126.com (H. Kou), sangge@caep.cn (G. Sang).

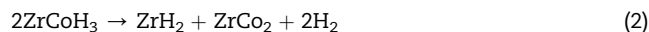
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fusion energy, the D-T gases are expected to be safely and efficiently stored and recovered in fusion reactor owing to the radioactivity and extremely expensive price of tritium [5,6]. The ZrCo alloy and DU (depleted uranium) are proposed as reference materials for recovery and delivery of hydrogen isotopes due to their low equilibrium dissociation pressure, fast hydrogen absorption rate and material stability for the storage of tritium [7–9]. Compared with DU, ZrCo alloy possesses such advantageous properties as non-radioactivation, low pyrophoricity, high hydrogen storage capacity, which thus has been proposed as candidate material by the ITER team for D-T storage according to reaction (1) [10–15].



As a result, extensive studies on the hydrogen storage properties of ZrCo alloy including thermodynamics, kinetics, hydrogen isotopes effect, disproportionation, etc., have been carried out [16–27]. Since it was discovered that the disproportionation of reaction (2) and reaction (3) would result in significant degradation of hydrogen storage properties of ZrCo alloy, the relevant issues to disproportionation come into the focus of research, which has been considered to be the biggest obstacle for wide application of ZrCo alloy to hydrogen isotopes storage [28–37].



Unfortunately, overcoming this problem seems a challenging task for there has been no effective way so far to thoroughly avoid or address the disproportionation of ZrCo alloy during the practical application process. Nevertheless, some studies demonstrated that Ti or Hf element substitution is a useful method to reduce the disproportionate rate and disproportionation extent of ZrCo alloy [38–43]. It was revealed that the improved anti-disproportionation property of Zr–Ti–Co or Zr–Hf–Co alloy is probably ascribed to the increase of equilibrium hydrogen pressure and the decrease of enthalpy change for reaction (1). These studies shed a bright light of hope into resolving the disproportionation issue of ZrCo alloy by adjusting the thermodynamic properties of ZrCo–H system. To achieve this, the first important thing evidently is to obtain the fundamental thermodynamic parameters of ZrCo–H system.

As well known, the enthalpy change and entropy change of hydrogenation and dehydrogenation reactions, which are very important thermodynamic parameters for the hydrogen storage materials, can be easily estimated by measuring the Pressure-Concentration-Isotherms (PCIs) according to Van't Hoff equation as following [44].

$$\frac{P}{P_0} = \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right) \quad (4)$$

where, R is gas constant, T is temperature, P_0 is standard pressure, P represents equilibrium pressure from PCI, ΔH is the enthalpy change and ΔS is the entropy change for the reaction. By measuring the PCI (Fig. 1), many studies have reported the ΔH and ΔS values for the normal hydrogenation/

dehydrogenation reaction of ZrCo alloy as shown in reaction (1) [45–51]. However, Devillers et al. [52] found that the equilibrium pressure could not be detected in the PCIs for the disproportionation reactions of ZrCo–H system, which can be explained by Fig. 1(b) and Fig. 1(c). It is clear from Fig. 1(b) that the ZrCoH_3 cannot stably exist at high temperature for measuring the PCI of reaction (2). Meanwhile, it can be seen from Fig. 1(c) that the equilibrium pressure cannot be obtained by measuring the PCI for the disproportionation shown reaction (3). Obviously, it seems impossible to estimate the ΔH and ΔS of disproportionation reactions for ZrCo–H system through measuring PCIs. As a result, the corresponding ΔH and ΔS of disproportionation reactions have never been provided by any report so far.

Therefore, an effort was made to estimate the ΔH and ΔS values for disproportionation reactions of ZrCo–H system by establishing the nonequilibrium phase boundaries in this work. This study will provide helpful guidance on avoiding disproportionation and improving anti-disproportionation property for ZrCo alloy during the application process.

Experimental

Sample preparation

ZrCo samples were provided by the General Research Institute for Nonferrous Metals (Beijing, China), in the form of granule with particle size of 2–4 mm. The activation processing and the corresponding hydrogenation/dehydrogenation measurements of the samples were performed by a Sievert's type apparatus. The typical activation procedures of ZrCo were conducted according to reference [53] by three steps including initial evacuation, hydrogenation and dehydrogenation. After activation, hydrogen absorption was carried out for the activated ZrCo samples to form ZrCoH_3 at room temperature under 1 bar hydrogen pressure for 12 h. For dehydrogenation, the ZrCoH_3 samples were heated from room temperature to 650 °C at a rate of 2 °C/min under different initial hydrogen pressures and then soaked at 650 °C for 1 h. For each time, about 1.5 g sample was loaded in the sample holder of the apparatus. Ordinarily, once the dehydrogenation experiments at different at different states were completed or the dehydrogenation experiment reached one desirable state, the valve of the sample holder was switched off and the samples were cooled to room temperature for XRD examination. Since the volume of the sample holder was very small, the residual hydrogen in the sample holder was not enough to incur the distinct phase transition during the cooling process. Consequently, the phase composition of the samples at different states was retained after cooling to room temperature.

X-ray diffraction

The crystal structure of ZrCo samples at different states in this study was characterized by X-ray powder diffraction (XRD) on a DX2700B diffractometer with Cu K_α radiation, 40 kV and 30 mA. The XRD patterns were measured in steps of 0.02° (2 θ) from 20° to 90° with a constant scanning rate of 0.6 s per step.

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