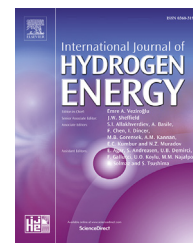




ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Kinetics of hydrogen desorption from titanium hydride under isothermal conditions

Mingwang Ma, Lei Wang, Binghua Tang, Ping Lyu, Wei Xiang, Yuan Wang, Xiaohua Tan*

Institute of Electronic Engineering, China Academy of Engineering Physics, Mianyang 621999, China

ARTICLE INFO

Article history:

Received 15 August 2017

Received in revised form

26 October 2017

Accepted 15 November 2017

Available online 6 December 2017

Keywords:

Titanium hydride

Thermal desorption spectroscopy

Desorption kinetics

Phase transformation

Phase diagram

ABSTRACT

Thermal desorption behaviours of titanium hydride powders under isothermal heat treatment conditions were studied using simultaneous thermogravimetry and thermal desorption spectroscopy (TG-TDS) method. The crystal structures and chemical compositions of the heat treated samples were investigated by X-ray diffraction analysis (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. It was found that the isothermal heating condition was of importance for the ordering of oxygen or surface oxidation. The phase transformation sequences during long time heating were established by combining the changing trends in the temperature/hydrogen content with the Ti–H phase diagram. A method for evaluating the kinetic parameters for different phase regions was proposed. The activation energies were calculated for these phase regions, and the corresponding rate-limiting steps were suggested.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Titanium hydride (TiH₂) is widely employed as a material for hydrogen storage, preparation of hydrogenated Ti alloy, bonding metals with non metals, producing porous Ti and especially as foaming agent to produce Al alloy foams [1–8]. All these applications involve the decomposition of TiH₂ or release of hydrogen through heat treatments under controlled atmospheres. For instance, the manufacturing process of Al alloy foams involves the addition of TiH₂ powder into molten Al alloy, generating hydrogen gas to foam the melt. A major drawback in this technique is the temperature mismatch between the Al alloy melting point and decomposition temperature of TiH₂ powder. It has been proposed by Matijasevic et al. [9] that the best recipe for a good foam involves: low-

melting Al alloy, pre-treated TiH₂ as blowing agent (usually pre-heated to temperatures between approximately 400 and 500 °C [9–12]), high heating rates without overheating, and so on. Understanding the hydrogen desorption characteristics of TiH₂ under different heat treatment conditions is essential for improving the pore morphologies and mechanical properties of Al alloy foams, as well as to develop new applications of TiH₂ [13–16].

To date, extensive studies of Ti–H system as well as of their dehydrogenation have been performed [17,18]. Thermal analysis techniques such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are commonly applied to investigate the dehydrogenation behaviours. Thermal desorption spectroscopy (TDS) is proved useful to identify the rate-controlling step of H₂ evolution and obtain the kinetic parameters. The

* Corresponding author.

E-mail address: caepiee@163.com (X. Tan).

<https://doi.org/10.1016/j.ijhydene.2017.11.103>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

simultaneous use of both thermal analysis and gas analysis techniques (TG-TDS, DSC-TDS, etc) provides the possibility of obtaining complete information on the thermodynamics and kinetic properties of metal hydrides [19–24]. For example, Fernández et al. [20] employed DSC-TDS technique to study the decomposition of TiH₂ powders and found a good correlation between hydrogen desorption and heat absorption. Matijasevic-Lux et al. [25] and Jiménez et al. [26] used TG-TDS to study the decomposition characteristics of TiH₂ powders by prior thermal and oxidizing pre-treatments. It was shown that TiH₂ started to release H₂ at approximately 380 °C accompanied by mass loss and heat treatment in air or argon delayed the onset temperature of hydrogen evolution.

Furthermore, phase transformation steps during TiH₂ dehydrogenation have also been proposed by many researchers and the results are still not consistent. According to Kennedy et al. [27], the two endothermic peaks of DSC trace indicated that the decomposition of TiH₂ powder in argon occurred in two stages, firstly the reduction in the stoichiometry of the hydride to δ -TiH_{1.5}, and secondly decomposition of the hydride to form the β and α phases. Bhosle et al. [28] found out that the two-step dehydrogenation process could be described as TiH₂ → TiH_x → α -Ti, where 0.7 < x < 1.1. Borchers et al. [29] recorded a three-peak structure TDS spectrum and assigned them to the ϵ → δ , δ → β and β → α phase transformation, respectively. Kudiiarov et al. [8] attributed the two peaks of hydrogen outflow to the hydride phase disintegration and α → β phase transition, respectively. Jiménez et al. [26] used in situ energy-dispersive XRD (ED-XRD) of white synchrotron radiation to study the decomposition of TiH₂ powder under different heating conditions in detail. The corresponding phase transformation sequence was obtained and expressed as δ → $\delta + \alpha$ → $\delta + \alpha + \beta$ → $\alpha + \beta$ → α under argon flow.

However, all the results mentioned above were conducted under non-isothermal heating conditions. Limited information is available on the decomposition behaviours of TiH₂ as well as their phase transformation sequences under isothermal heat treatment conditions [25]. The isothermal hydrogen desorption kinetics of TiH₂ are needed to be further elaborated by considering the following situations. Firstly, during the pre-heat treatments, TiH₂ is heated to the selected temperatures and then held there for a long duration. Secondly, during the foaming process the TiH₂ blowing agent is added into the molten Al alloy and then held there for a short time. It is believed that the thermal decomposition characteristics of TiH₂ have a close relationship with the pore structure of the Al alloy foam. Therefore, it is of great importance for understanding the hydrogen evolution behaviours during long heating duration and the change of the state after isothermal processing.

In this work, the kinetics of hydrogen desorption from TiH₂ under isothermal conditions is explored. The phase transformation sequences and the corresponding kinetic parameters are determined. The holding temperatures were selected from the following points of view. On one hand, the pre-heat treating temperatures of TiH₂ are between approximately 400 and 500 °C [9–12]. On the other hand, the solidus and liquidus temperatures of typical Al alloys are in the range of 525–660 °C [9]. Therefore, the isothermal desorption behaviours of TiH₂

were conducted in the temperature range of 400–660 °C in this study.

Experimental

Commercial TiH₂ powder (99% pure), with the mean size of about 8 μ m [30], was used in this study. The isothermal decompositions of TiH₂ were conducted by TG-TDS (IGA-003, Hiden, UK). The samples with a weight of approximately 150 mg were heated up at a linear temperature ramp of 10 °C/min to the chosen temperatures, namely, 400, 450, 500, 550, 600 and 660 °C, and then kept for nearly 1000 min. The emitted H₂ was measured using a quadrupole mass spectrometer (QMS) connected to IGA-003 through a thin capillary tube that was heated to 200 °C to avoid vapor condensation. The decomposition measurements were performed under pure Ar gas ($\geq 99.999\%$) flow conditions at the pressure of 1 atm with a flow rate of 50 ml/min. The residual H/Ti atom ratios were calculated from the mass losses obtained from TG measurements.

The crystal structures were identified by XRD (Rigaku D/Max-2400) using Cu-K α radiation, at a scanning rate of 4°/min with a generator voltage of 40 kV and current of 150 mA. All XRD measurements were performed at room temperature and the phase compositions were determined on the basis of JCPDS files provided by the International Center for Diffraction Data. Quantitative phase analysis was performed using the Rietveld refinement method. The experimental patterns were fitted with a linear combination of the theoretical patterns and of the background using optimized values of lattice parameters and parameters of broadening the diffraction maxima of phases.

The surface characterizations of the as-received and heat treated TiH₂ powders were analysed using X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Kratos) with a monochromatic Al K α (1486.6 eV) line of an X-ray source. The photoelectron peaks were fitted using a mix of Gaussian and Lorentzian forms, and the background was determined by the Shirley method.

Results and discussion

Powder characteristics

The phase compositions of samples heated under argon flow with the duration of approximately 1000 min at different temperatures were determined by XRD after cooled to room temperature, which are marked in Fig. 1. The corresponding XRD data are summarized in Table 1. The as-received titanium hydride containing nearly 1.97 H/Ti is identified as the δ phase with lattice constant $a = 0.4452$ nm. The δ hydride has a fcc structure, CaF₂-type, in which hydrogen occupies tetrahedral positions [31,32]. After the isothermal treatment at 400 °C for 1000 min under argon pressure of 1 atm, the sample contains 1.51 H/Ti and shows the co-existence of δ -TiH_{1.5}, γ -TiH and Ti₃O. The phase of δ -TiH_{1.5} is the major composition, which is the minimum stoichiometry for the δ phase [27]. Neutron diffraction shows that for the δ -TiH_{1.5} the hydrogen atoms are

Download English Version:

<https://daneshyari.com/en/article/7708318>

Download Persian Version:

<https://daneshyari.com/article/7708318>

[Daneshyari.com](https://daneshyari.com)