Progress in Natural Science: Materials International xxx (xxxx) xxx–xxx

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Contents lists available at ScienceDirect

Progress in Natural Science: Materials International

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

Original Research

Experimental investigation and thermodynamic assessment of the yttrium-hydrogen binary system

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ARTICLE INFO

Keywords:
Rare earth
Yttrium
Hydrogen
Pressure composition isotherm
Phase diagram
Thermodynamics

ABSTRACT

A coupled experimental investigation and thermodynamic study of the yttrium-hydrogen (Y-H) binary system were carried out to provide more comprehensive and quantitative insights into the key thermodynamic properties of this system. Y-H system in the full range of H/Y = 0–3.0 was investigated by accurate pressure composition isotherm (PCI) measurement to provide credible phase equilibria information and thermodynamic data. The phase boundaries obtained were in agreement with previous experimental data but with improved accuracy. With the guide of the crystal structures, all the solid phases were modelled using the three sublattice model. The Y-H phase diagram and thermodynamic parameters were calculated and assessed with the CALPHAD technique. The obtained results are in very good agreement with our experimental data and the published data reported in literature. The obtained thermodynamic database of Y-H system can be used to predict the hydrogenation behavior and decomposition temperatures of hydrides.

1. Introduction

Motivated by the need to develop new and clean energy technologies, binary Y-H system has gained great interests in both academia and industry communities. The change in the optical properties of Y thin films upon exposure to H_2 allows us to create eye-visible effects that has the potential to be used for H_2 sensing applications [1,2]. The fine yttrium hydride obtained by hydrogenating the Mg-Ni-Y long-period stacking ordered (LPSO) structure is found to enhance remarkably the kinetics of the subsequent hydrogen absorption/desorption [3,4]. More recently, new and rapidly evolving discoveries have positioned Y-H compound as highly promising materials for future electrochemical energy storage, such as thin film electrode of direct borohydride fuel cells (DBFCs) [5–7]. It can be seen that the thermodynamic properties of Y-H compounds are of great importance and become the base to describe the absorption/desorption processes of multicomponent alloy from thermodynamic aspect. A reliable thermodynamic description and related theoretical analysis of Y-H system is quite useful for the design of materials. However, there is lack of a complete thermodynamic evaluation of this system.

The CALPHAD (Calculation of phase diagrams) method is an extensively used semi-empirical technique for phase diagram calculation and modeling [8]. It consists in describing the Gibbs energies of the different phases present in a system by adjusting thermodynamic parameters. The parameters involved in the models are optimized on the basis on experimental data and the phase diagram information from the literature. For various Metal-Hydrogen systems [9–12], the best approach to obtain thermodynamic data and deduce partial phase diagram is the accurate and detailed measurement of pressure composition isotherms (PCI) curves [13–17]. However, the uncertainty in the significance of the thermodynamic properties and the phase equilibrium is compounded by the fact that the reported values for the Y-H system do not agree well with each other [18–21]. The difference is due to the fact that the content of gaseous impurities like oxygen or nitrogen in raw materials would significantly affect the PCI curves [20].

Y-H system has a phase diagram which is somewhat similar to those of the heavy rare earth-hydrogen (e.g., Gd-H, Dy-H and Er-H) systems [14–16]. Metallic yttrium has a hexagonal-close-packed (hcp) structure at low temperature and transforms into a body centered cubic (bcc) structure at 1478 °C [18]. A particularly intriguing characteristic is that the solubility limit in the solid solutions (α-Y) can up to a very high atomic concentration (H/Y = 0.235) even at room temperature [18,22,23]. The low temperature solid solution α*phase with a short-range ordered structure has not been considered in this work because it

Peer review under responsibility of Chinese Materials Research Society.
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https://doi.org/10.1016/j.pnsc.2018.04.001
Received 13 November 2017; Received in revised form 15 March 2018; Accepted 10 April 2018

is metastable [24,25]. Two nonstoichiometric hydride phases are stable in Y-H system: face-centered-cubic (fcc) dihydride (β-$YH_{2\pm x}$) with CaF_2 crystal structure and hcp trihydride (γ-YH_{3-y}) with HoD_3 crystal structure [26,27].

Some PCI measurements have been made and reported in the literature. Between the solid solution and the dihydride, the PCI measurements of Y-H system have been carried out at various temperatures ranging from 600 °C to 1300 °C [19–21]. The reported phase boundaries, however, are scattered within a narrow region and do not agree well with each other. It was found that the content of gaseous impurities like oxygen or nitrogen in Y metal would significantly affect the accuracy of PCI measurements [20]. Between the dihydride and the trihydride, the only available data are from Ref. [21] and the absence of adequate experimental points on their isotherms limits our judgment on identifying phase boundaries. The experimental Y-H binary phase diagram from Ref. [18] is roughly drawn through the averages of the above data without discrimination. Therefore, accurate PCI curves are required to identify the plateau regions and phase boundaries.

The hydrogen solubility limits of the Y metal were determined by Beaudry et al. [23] through equilibration analytical technique between 25 °C and 850 °C. Bonnet et al. [22] also determined the terminal hydrogen solubility by accurate resistivity differences measurement.

Herein, we obtain thermodynamic data and phase equilibria information of the Y-H system by means of PCI measurement using high purity raw materials, precision Sievert apparatus and accurate operation. In addition, we compile all the available experimental information, to confirm its consistency and to create an optimized set of data by using the CALPHAD approach. The calculated phase equilibria and thermodynamic quantities agree well with experimental data.

2. Experimental

To obtain accurate PCI curves, there must be high purity raw materials, precision Sievert apparatus and accurate operation.

The raw material used in the paper was high purity yttrium ingots purified by vacuum distillation. The oxygen and nitrogen impurities concentration could be decreased to 0.0155 wt% and 0.0030 wt% after purification, which are the highest purities reported.

The PCI measurement was carried out in a home designed stainless steel constant-volume Sieverts apparatus, the detail of which has been described previously [15,16]. Before measurement, a Y ingot ~ 0.5 g was loaded into a tungsten foil boat. The hydrogen atoms could pass through the loose rare earth oxide layer, and then diffused into the metallic layer underneath with the excellent hydrogen absorption kinetics. So the hydrogen absorption curves of high purity Y can be measured without any activation treatment. For RE-H system, desorption isotherms are very hard to be measured because of the long equilibrium times. Therefore, the most of the PCI curves of the RE-H binary systems were investigated only by hydrogen absorption measurements. Between the solid solution α-Y and the β-$YH_{2\pm x}$, the PCI curves were measured at six different temperatures from 650 °C to 900 °C. In addition, PCI measurements corresponding to the two hydrides were carried out at five different temperature from 250 °C to 350 °C. The hydrogen dosing was manually controlled using a needle valve and carefully adjusted to identify the limits of the plateau regions and corresponding phase boundaries. The equilibrium hydrogen pressure data were recorded by a computer controlled data acquisition system after the pressure reached constant for at least 0.5 h. The reliability and accuracy of this system was proved by our previous work. The reproducibility of all the PCI curves was confirmed by measuring them more than once.

Samples with different H/Y ratio could be obtained by controlling the total gas intake elaborately. After the chamber was cooled down to room temperature, the samples with different hydrogen contents are analyzed by X-ray Diffraction (XRD, PA Nalytical X'Pert3 Powder, Cu Kα, 2°/min). Differential scanning calorimetry (DSC, Netzsch 204 HP calorimeter) measurements of YH_3 powders was carried out in a hydrogen gas flow (99.999%, 50 mL min^{-1}) with various pressures.

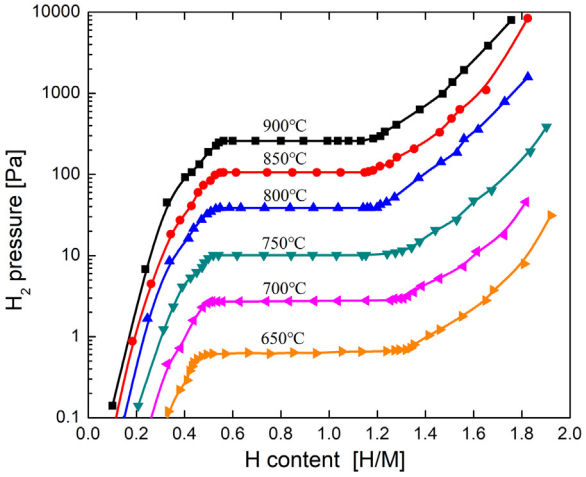

Fig. 1. Pressure-composition absorption isotherms measured from 650 °C to 900 °C in H/Y = 0.0 − 2.0 (from α-Y to β-$YH_{2\pm x}$).

Finally, the Y-H binary phase diagram was assessed with the CALPHAD method using the Pandat phase equilibrium calculation software.

3. Experimental results and discussion

3.1. Pressure-composition-isotherms

All the PCI curves were measured during the first hydrogen absorption cycle without any activation process. In our measurement, the hydrogen dosing was elaborately controlled so that the phase equilibria data were more accurately determined compared to previous studies. The PCI curves in the composition region from pure Y metal to the dihydride phase were measured at various temperatures from 650 °C to 900 °C, as shown in Fig. 1. A well defined plateau corresponding to the transformation from α-Y to β-$YH_{2\pm x}$ was observed for each temperature. The width of the plateau shrinks gradually with increasing temperature, indicating the contour variation of the α-Y/β-$YH_{2\pm x}$ biphasic region. The above features shows a decided similarity to the heavy rare earth-hydrogen system, in particular Gd-H and Dy-H systems [15,16].

As shown in Fig. 2, a second two-phase plateau region between the two hydrides was observed at lower temperatures (from 250 °C to 350 °C) because the trihydride phase became unstable above this range.

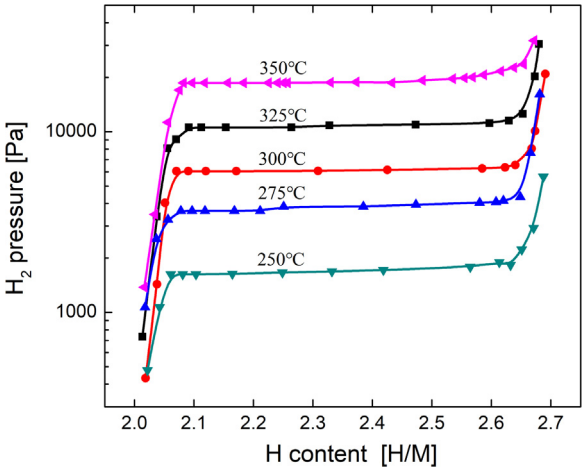

Fig. 2. Pressure-composition absorption isotherms measured from 250 °C to 325 °C in H/Y = 2.0 − 3.0 (from β-$YH_{2\pm x}$ to γ-YH_{3-y}).