Journal of Alloys and Compounds 706 (2017) 520–525

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

P–V–T relation of the Fe–H system under hydrogen pressure of several gigapascals

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ARTICLE INFO

Article history:
Received 15 May 2016
Received in revised form
17 February 2017
Accepted 18 February 2017
Available online 21 February 2017

Keywords:
Iron–hydrogen solid solution
Miscibility gap
Synchrotron X-ray diffraction

ABSTRACT

We have measured the volumes of dhcp- and fcc-FeH_x at temperatures of 300–950 K and hydrogen pressures of 4–7 GPa using in situ X-ray diffraction. For fcc-FeH_x, the expanded volumes per Fe atom with respect to fcc-Fe metal were converted to hydrogen compositions x using hydrogen-induced volume expansion v_H. A miscibility gap in the x–T diagram of fcc-FeH_x was confirmed to be in agreement with an earlier study, and the critical pressure was located in a rather narrow span of 4.0–4.5 GPa with a critical composition of x = ~0.4. We examined Arrhenius plot analysis of the x–T relations to derive the enthalpy of solution of hydrogen ΔH_s. However, an irregular behavior of the x–T relations did not allow derivation of a reliable value of ΔH_s.

1. Introduction

Iron, a prototype of ferromagnetic transition metal, forms hydrides at high hydrogen pressures, and its structural and magnetic properties have been intensively studied using X-ray and neutron diffraction [1–8], Mössbauer spectroscopy, magnetization, and X-ray absorption spectroscopy [9–14]. An outline of the Fe–H phase diagram up to 2000 K and 10 GPa is shown in Fig. 1 [15–18]. The α phase is a ferromagnetic solid solution wherein the metal atoms form a bcc structure. A high pressure ε' phase wherein the metal atoms occupy the vertexes of the dhcp lattice has a hydrogen composition of x = ~1 at an ambient temperature (hereafter referred to dhcp-FeH_x). In contrast to the nonmagnetic feature of the high-pressure hcp phase of iron, dhcp-FeH_x is ferromagnetic. A high-temperature γ phase is a solid solution wherein the metal atoms form an fcc structure (hereafter referred to fcc-FeH_x). As the hydrogen composition increases with hydrogen pressure and oppositely decreases with temperature, the terminal solubility is expected to extend up to ~1 through the temperature and pressure range shown in Fig. 1.

Phase separation has earlier been reported for fcc-FeH_x solid solution [18]. The phase separation or the miscibility gap is characterized as a specific region in an x–T diagram, where solid solutions of two different hydrogen compositions coexist. This phase separation is attributed to the long-range hydrogen–hydrogen interactions. For fcc-FeH_x, theoretical calculations have predicted the appearance of a miscibility gap at 4–5 GPa with a critical point of 560 K and 4.5 GPa [19]. The$V$–T relations measured for fcc-FeH_x using in situ synchrotron X-ray diffraction under high temperatures and pressures revealed the possible presence of a miscibility gap in the predicted P–T region; however, the gap boundary and critical point were not convincingly determined [18].

Neutron diffraction measurement is the most effective experimental technique for determining the hydrogen composition of the Fe–H/D system. A high-temperature and high-pressure neutron diffraction technique was developed using a multi-anvil high-pressure apparatus and was applied to a structural investigation on fcc-FeD_x at around 6 GPa [20]. The site occupancies of deuterium atoms were successfully determined at 988 K and 6.3 GPa. The in situ neutron diffraction measurement, however, is still not yet a conventional method for a phase study as it requires the scanning of P–T paths over a wide temperature and pressure spans; it takes several hours to collect one diffraction profile with high statistics sufficient for a precise structural analysis.

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http://dx.doi.org/10.1016/j.jallcom.2017.02.209
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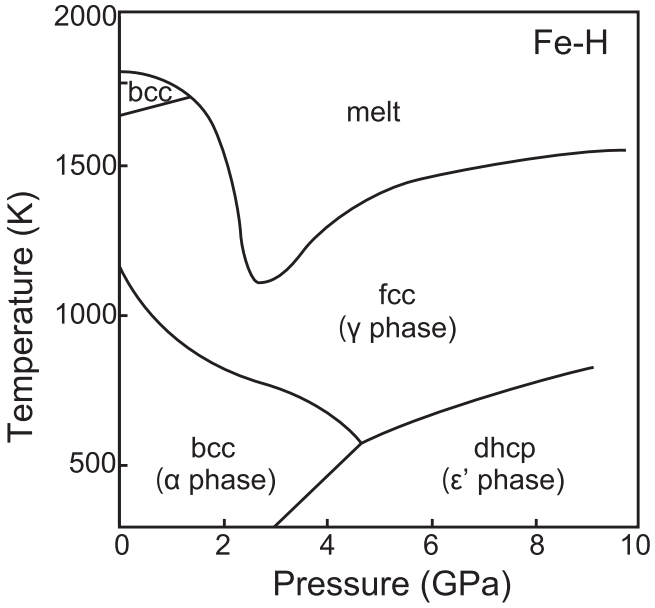

Fig. 1. Outline of phase diagram of Fe–H system in a temperature range of 300–1000 K and a pressure range of 0–10 GPa [1–7].

The aim of this study was to investigate the pressure–volume–temperature, *P–V–T*, relations for dhcp- and fcc-FeH_x at temperatures of 300–950 K and hydrogen pressures of 4–7 GPa using in situ synchrotron X-ray diffraction. For fcc-FeH_x, hydrogen compositions x were converted from the measured expanding volumes of fcc-FeH_x with a hydrogen-induced volume expansion v_H recently determined by the neutron diffraction measurement [20]. Using the x–T relations. we attempted to relocate the boundary of the miscibility gap and derive an enthalpy of solution of hydrogen ΔH_s.

2. Experimental section

The starting material was reagent-grade pure-iron flakes (purity: 99.9%) with a particle lateral size of less than 100 μm and a thickness of less than 20 μm. The flakes were mixed with BN powder (purity: 99% and grain size: >10 μm) with a volume ratio of 2:3 to prevent grain growth of iron at high temperatures. The mixture was compacted into a disk measuring 0.5 mm in diameter and 0.2 mm in height, which was loaded into a sleeve made of pyrolytic boron nitride.

High pressures and temperatures were generated using a cubic-type multi-anvil press. Hydrogenation of the specimen was achieved by using a high-pressure cell originally designed by Fukai and Okuma [21]. Fig. 2 shows the high-pressure cell assembly used in the present study. We employed a compacted disk of AlH_3 as an internal hydrogen source, which decomposed into fluid hydrogen and aluminum metal upon heating above 800 K. Fluid hydrogen encapsulated in a NaCl capsule reacted with the Fe specimen to form FeH_x. The temperature was monitored using Pt/Pt–13 Rh thermocouples with an uncertainty of less than 20 K. As reported in our earlier study [20], elemental analysis had been performed for a recovered iron specimen that reacted with hydrogen to form a solid solution at high P–T conditions. The amounts of impurities of Na, Cl, etc. were on the order of thousands of ppm and their influence on the Fe–H system was considered to be negligible.

The structural changes due to hydrogenation of the iron specimen and further the dhcp-fcc phase transition of FeH_x were observed on heating and cooling runs along approximately isobaric

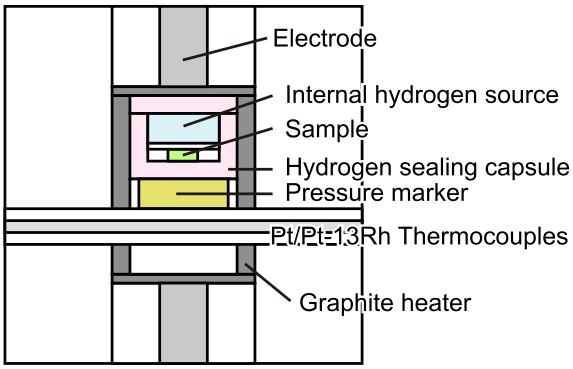

Fig. 2. Schematic of a high-pressure cell assembly used for in situ X-ray diffraction measurements on the Fe–H solid solution at temperatures of up to 1000 K and pressures of up to 7 GPa.

paths using an in-situ synchrotron-radiation powder X-ray diffraction technique. White X-rays generated from a bending magnet source were irradiated on the specimen and diffracted X-rays were detected with a solid-state detector in an energy dispersive mode. The pressure was calculated from the measured unit cell volume of NaCl using the isotherm calculated by Decker et al. [22]. Details on the high pressure generation, hydrogenation cell, and in situ synchrotron-radiation powder X-ray diffraction technique are described elsewhere [23].

Fig. 3 shows the pressure–temperature path, along which time-resolved X-ray diffraction profiles were collected. The specimen was first pressurized to 7.76 GPa at room temperature and was heated to 818 K at a rate of 25 K/min under a constant ram load. The specimen was then cooled to room temperature at a rate of 25 K/min. Powder X-ray diffraction profiles were recorded continuously with a 12 s integration time during the heating and cooling processes. X-ray diffraction measurements were performed for heating and cooling cycles at several pressures between 4 and 7 GPa, and their run numbers and P–T conditions are summarized in Table 1.

The heating and cooling rates were carefully examined to achieve the formation of a nearly homogeneous Fe–H solid solution within the integration time of the X-ray diffraction measurements.

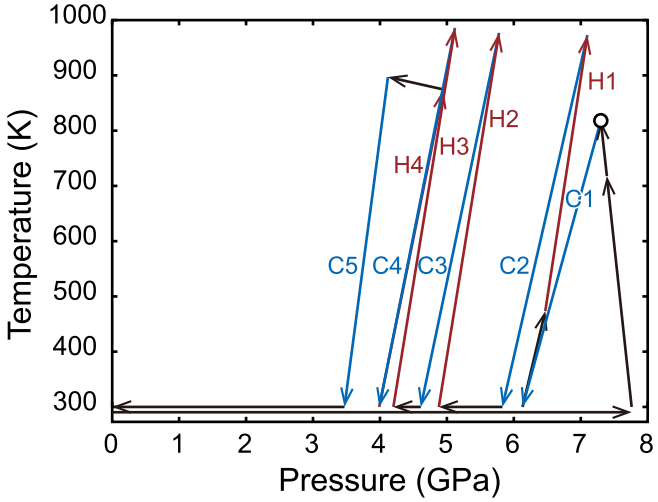

Fig. 3. Pressure-temperature paths for in situ X-ray diffraction measurements. Iron specimen was hydrogenated at 7.3 GPa and 818 K, where an internal hydrogen source decomposed and evolved hydrogen (open circle). The pressures were measured at each starting and ending point indicated with arrows. Those between starting and ending points were calculated from linear interpolations.