

The phase diagram and superabundant vacancy formation in Fe–H alloys revisited

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Abstract

Detailed measurements of the $p(\text{H}_2)$ – x – T relation in the fcc phase of Fe–H alloys revealed the characteristics of supercritical anomalies, with the critical point located at around a hydrogen pressure of 4–5 GPa and a temperature of 400 ± 100 °C. The vacancy–hydrogen (Vac–H) cluster concentration in the fcc phase estimated from the lattice contraction was proportional to the hydrogen concentration independently of temperature and hydrogen pressure. A small lattice contraction due to the superabundant vacancy formation was also observed in the bcc phase, in accordance with previous thermal desorption measurements, and showed a similar dependence on the hydrogen concentration. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Gradual lattice contractions were observed over several hours in many metals when the samples were held at high temperatures and high hydrogen pressures [1–5]. This phenomenon has been ascribed to the formation of a large number of metal atom vacancies, caused by the reduction of formation energy of vacancies by trapping hydrogen atoms. The concentration of vacancy–hydrogen (Vac–H) clusters, thus formed, in the fcc phase of various metals amounted to 9 at.% in Cr–H [1], 10 at.% in Mn–H [2], 11 at.% in Pd–H [3] and 30 at.% in Ni–H [4], many orders of magnitudes larger than the vacancy concentrations under ordinary conditions.

For the Fe–H alloys, the $p(\text{H}_2)$ – T phase diagram (Fig. 1) was constructed by Fukai et al. [5] over wide ranges of temperature and hydrogen pressure, including the data reported earlier by other authors [6–8]. The main features of the diagram are a rapid descent of the melting point with increasing hydrogen pressure to 3 GPa and the appearance of dhcp (ϵ) hydride at higher pressures. The triple point

$\alpha + \gamma + \epsilon$ is located at 5 GPa and 300 °C. Regarding the superabundant vacancy (SAV) formation, the concentration of SAVs in the fcc phase at 896 and 784 °C under 5 GPa [5] is approximately the same as in other fcc metals quoted above [1–4]. In the bcc phase, thermal desorption (TDS) measurements after heat treatments at 200–600 °C under $p(\text{H}_2) = 1.7$ GPa revealed the presence of 0.1–1.2 at.% hydrogen trapped by vacancies [9], an order of magnitude smaller than in the fcc phase. A similar concentration of SAVs was also observed in other bcc alloys, Nb–H [10] and Mo–H [11].

The purpose of this work is two-fold: (1) to study the $p(\text{H}_2)$ – x – T relation in the fcc phase and (2) to study the relation between the concentrations of Vac–H clusters and hydrogen in both bcc and fcc phases.

2. Experimental methods

Powder samples of 99.98% Fe (#400 mesh) were formed into pellets of $\text{Ø} 1 \times (2\text{--}3)$ mm, encased in a capsule of NaCl together with an internal hydrogen source (LiAlH_4), and placed at the center of a high-pressure cell (a cube of 8 mm in edge length) made of amorphous boron–epoxy resin composite. The temperature could be raised to 1000 °C by passing a current in a graphite tube heater around the capsule, and H_2

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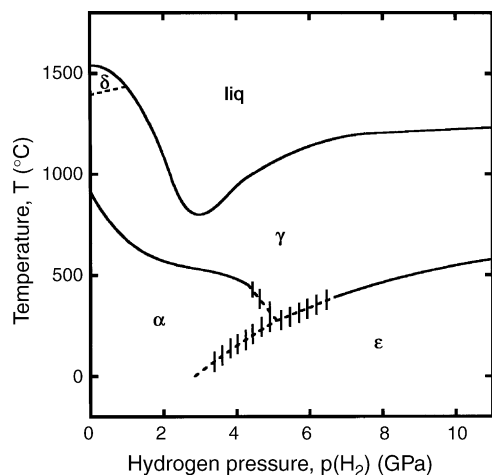


Fig. 1. The $p(\text{H}_2)$ - T phase diagram of the Fe-H system. α and δ are low-concentration hydrogen solutions in bcc Fe; γ and ϵ are fcc and dhcp hydrides, respectively.

was supplied to the sample at $\sim 300^\circ\text{C}$ by decomposition of the hydrogen source.

The XRD was measured at a synchrotron radiation source in Tsukuba, using a cubic-anvil press MAX80. This apparatus compresses the cubic sample cell from six perpendicular directions and produces up to ~ 7 GPa at the center of the cell. The actual pressure was determined from the lattice parameter of NaCl using a Decker scale [12]. The energy-dispersive method was adopted: an SSD was placed at a fixed angle from the incident X-ray beam and the diffracted X-rays were energy-analyzed. A measuring time of each XRD pattern was 1–5 min.

The temporal variation of the lattice parameter occurs in two different time scales. The lattice expansion caused by dissolution of hydrogen should be very fast and the equilibrium should be reached before the first XRD pattern could be measured. Subsequently, the lattice contraction due to SAV formation occurs over a longer period time, long enough to be followed by XRD measurements.

3. Experimental results and discussions

3.1. Dependence of the hydrogen concentration on temperature and hydrogen pressure

The dependence of the atomic volume (volume per FeH_x) on temperature and hydrogen pressure at $T = 650$ – 1050°C and $p(\text{H}_2) = 2.5$ – 6 GPa is shown in Fig. 2. These data were measured immediately after the temperature was set at a prescribed value (before the lattice contraction due to SAV formation set in). In comparison to the atomic volume of pure Fe under corresponding conditions [13–16], the volume increase due to hydrogen dissolution at any given temperature increases with increasing hydrogen pressure.

The $p(\text{H}_2)$ - x - T relation constructed from Fig. 2 is shown in Fig. 3. The hydrogen concentration is estimated from the

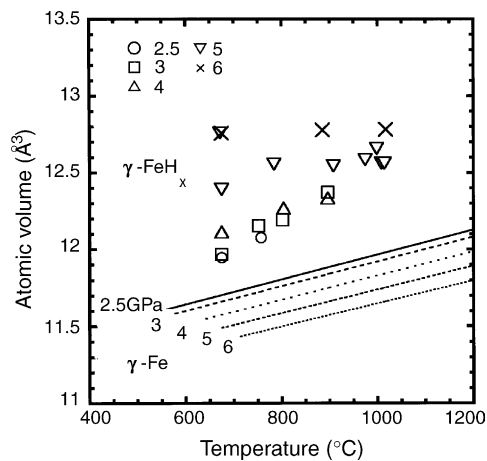


Fig. 2. The $p(\text{H}_2)$, T dependence of the atomic volume (volume per FeH_x) in the fcc phase. The corresponding dependence for fcc (γ) Fe [13–16] is also shown for comparison. The pressure implies hydrogen pressure for FeH_x and a simple mechanical pressure for Fe.

observed initial increase $\Delta\Omega$ of the atomic volume using the expression:

$$x_{\text{H}} = \frac{\Delta\Omega}{\Omega_{\text{H}}}$$

where $\Omega_{\text{H}} = 1.9 \text{ \AA}^3$ [17]¹ is the increment of the atomic volume per unit concentration of hydrogen. The figure shows that the hydrogen concentration increases with increasing temperature at $p(\text{H}_2) \leq 4$ GPa, but decreases with increasing temperature at $p(\text{H}_2) \geq 5$ GPa. This changeover from the endothermic to exothermic process of dissolution is clearly a supercritical anomaly. The critical point can be roughly located at a hydrogen pressure of $p_{\text{c}}(\text{H}_2) = 4$ – 5 GPa, and a temperature well below the lowest temperature of the measurements, probably at $T_{\text{c}} = 400 \pm 100^\circ\text{C}$ close to the bcc-fcc phase boundary. This is consistent with the thermodynamical calculation of Sugimoto and Fukai ($p_{\text{c}}(\text{H}_2) \sim 4.5$ GPa and $T_{\text{c}} \sim 270 \pm 50^\circ\text{C}$) [18], and also with the critical temperatures observed in the fcc hydride phase of neighboring metals; $T_{\text{c}} \leq 300^\circ\text{C}$ in the Co-H system [19] and $T_{\text{c}} = 390^\circ\text{C}$ [20] and 360°C [21] in the Ni-H system.

3.2. Superabundant vacancy formation in the fcc phase

The XRD was measured at $p(\text{H}_2) = 2.5$ – 6 GPa and $T = 750$ – 1050°C , at short intervals to delineate the temporal variation of the lattice parameter. A representative variation of the lattice parameter is shown in Fig. 4. The initial value of the lattice parameter is much larger (by 0.8 \AA) than that of pure Fe under the same p , T condition (3.61 \AA) due to the dissolution of hydrogen. From this initial volume increment, the hydrogen concentration is estimated as $x_{\text{H}} = 0.43$. The

¹ A value obtained for the fcc alloy $\text{Fe}_{0.65}\text{Mn}_{0.29}\text{Ni}_{0.06}\text{H}_{0.95}$.

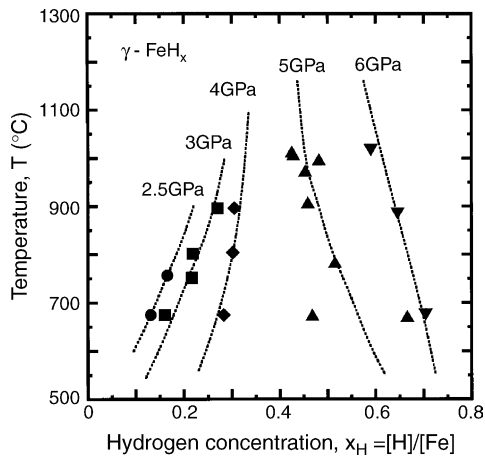


Fig. 3. The $p(\text{H}_2)$ - x - T relation of the Fe-H system in the fcc phase.

concentration of Vac-H clusters, on the other hand, can be estimated using the expression:

$$x_{\text{cl}} = \frac{3\Delta a/a_0}{v_{\text{R}}^{\text{cl}}/\Omega}$$

where $3\Delta a/a_0$ represents the change of the atomic volume caused by the Vac-H clusters, and v_{R}^{cl} is the relaxation volume of a Vac-H cluster. Lacking knowledge of this quantity, here we adopt a value of $v_{\text{R}}^{\text{cl}}/\Omega = -0.36$, an average of the calculated relaxation volumes of vacancies for a large number of metals [22]. In the example of Fig. 4, the Vac-H cluster concentration is estimated as $x_{\text{cl}} = 0.13$.

The relation between the concentrations of hydrogen and Vac-H clusters is shown in Fig. 5, where the previous data of Mori and co-workers [5] are also included. The Vac-H cluster concentration is nearly proportional to the hydrogen concentration independently of the temperature and hydrogen pressure. Very similar results have been obtained for Ni and Co [23].

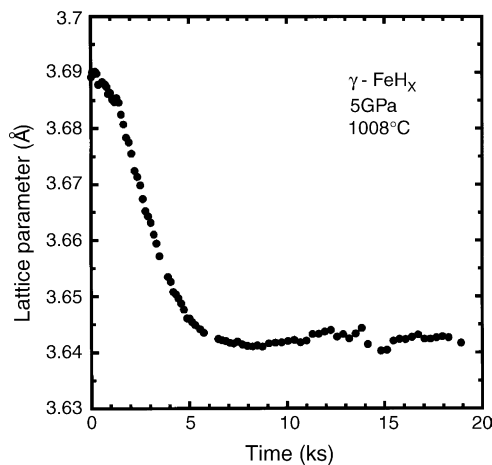


Fig. 4. Temporal variation of the lattice parameter of Fe-H alloys in the fcc phase at $p(\text{H}_2) = 5$ GPa and $T = 1008$ °C.

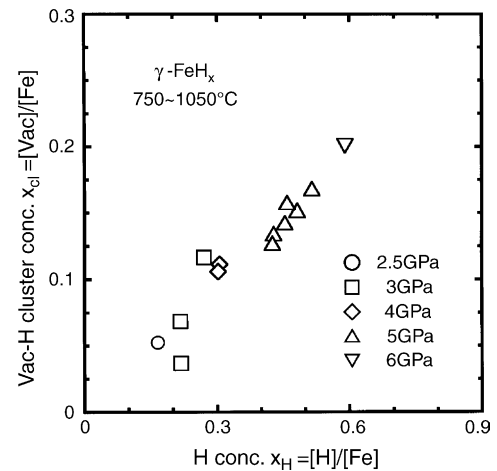


Fig. 5. The relation between the concentrations of hydrogen and Vac-H clusters in the fcc phase.

3.3. Superabundant vacancy formation in the bcc phase

The XRD from the bcc phase was measured at $p(\text{H}_2) = 2$ –4 GPa and $T = 200$ –400 °C. The observed initial volume increment is shown in Fig. 6, together with the data for pure Fe. The latter includes previous data of Mao et al. [13], Manghani et al. [14] and Boehler et al. [15,16], supplemented with our measurements at 1.5–3.5 GPa. The increase of atomic volume due to hydrogen dissolution is much smaller than in the fcc phase (Fig. 2).

An example of the lattice contraction measurements at $p(\text{H}_2) = 3.3$ GPa and $T = 303$ °C is shown in Fig. 7. Compared with the fcc phase, the observed contraction is at least an order of magnitude smaller. Again using $\Omega_{\text{H}} = 1.9 \text{ \AA}^3$ and $v_{\text{R}}^{\text{cl}}/\Omega = -0.36$, the concentrations of hydrogen and Vac-H cluster are estimated to be $x_{\text{H}} = 5.3 \times 10^{-2}$ and $x_{\text{cl}} = 0.28 \times 10^{-2}$, respectively.

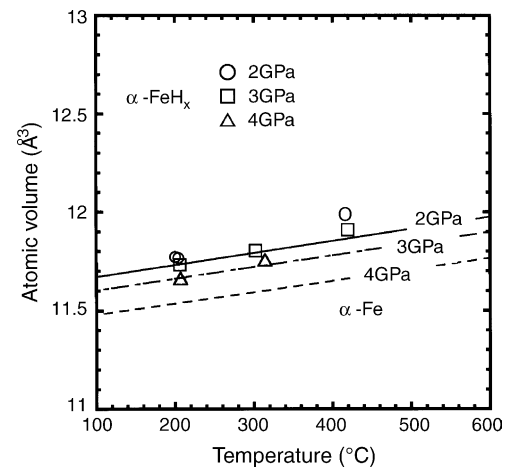


Fig. 6. The $p(\text{H}_2)$, T dependence of the atomic volume (volume per FeH_x) in the bcc phase. The corresponding dependence for bcc (α) Fe [13–16] is also shown for comparison. The horizontal axis implies hydrogen pressure for FeH_x and a simple mechanical pressure for Fe.

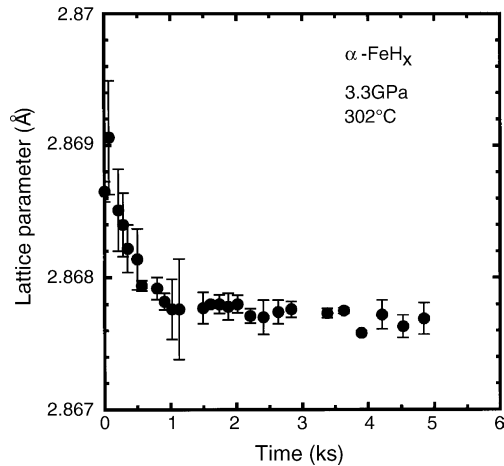


Fig. 7. Temporal variation of the lattice parameter of Fe–H alloys in the bcc phase at $p(\text{H}_2) = 3.3$ GPa and $T = 302$ °C.

The relation between the concentrations of hydrogen and Vac–H clusters obtained at $p(\text{H}_2) = 2\text{--}4$ GPa and $T = 200\text{--}400$ °C is shown in Fig. 8. The results of previous TDS measurements in the bcc phase [9] are also included. In that work, the hydrogen concentration was estimated using the result of thermodynamical calculations $x_{\text{H}} \approx 1.6 e^{-0.29 \text{ eV}/kT}$ [18] appropriate for $p(\text{H}_2) = 1.7$ GPa, and the Vac–H cluster concentration was obtained by dividing the concentration of the desorbed (trapped) hydrogen by 6. Although the scatter of the data points is large, the XRD and TDS results are consistent with each other. The uncertainty in the relaxation volume may affect the absolute values of the Vac–H cluster concentrations estimated in the present work, but it does not affect the overall trend.

Within the scatter of the data points, we may conclude that the linear dependence of x_{cl} on x_{H} holds not only in the fcc phase but also in the bcc phase. A similar relation was observed in the fcc phase of Ni–H and Co–H alloys [23] and in the bcc phase of Nb–H alloys [10].

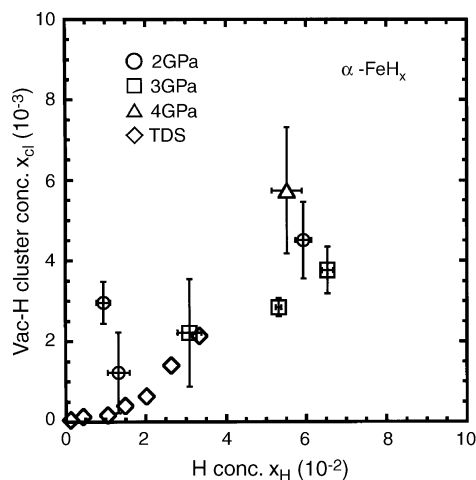


Fig. 8. The relation between the concentrations of hydrogen and Vac–H clusters in the bcc phase. Results obtained from TDS measurements [9] are also shown for comparison.

4. Summary and conclusions

From in situ XRD measurements at high temperatures and high hydrogen pressures, the $p(\text{H}_2)\text{--}x\text{--}T$ relation in the fcc phase was determined, and the lattice contraction due to the superabundant vacancy formation was measured both in the fcc and bcc phases as a function of $p(\text{H}_2)$, x , T . In the fcc phase, the concentration of Vac–H clusters was found to be proportional to the hydrogen concentration, independently of the temperature and hydrogen pressure. Nearly the same trend was observed in the bcc phase.

Acknowledgements

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