Superabundant Vacancy Formation in Iron under High Hydrogen Pressures: Thermal Desorption Spectroscopy

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Thermal desorption of hydrogen from high-purity iron was observed after heat treatments at 470–870 K under a hydrogen pressure of 1.7 GPa. A total of 0.1–1.5 at% trapped hydrogen, with its amount increasing at higher holding temperatures, was desorbed in five stages. The most prominent one, occurring at 400–440 K, was identified as being due to the release from vacancy-hydrogen complexes, VacH₆. The binding energy of a vacancy is estimated to be 44 ± 4 kJ/mol.

Possible implications of the result for hydrogen embrittlement are discussed.

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I. Introduction

Due to low solubilities and high diffusivities, most of hydrogen atoms once dissolved in an iron lattice by *e.g.* electrolytic charging are quickly desorbed at room temperature, leaving only a small fraction in the form of bubbles or complexes with existing lattice defects. Understanding the behavior of these trapped hydrogen atoms in iron is particularly important because some of them gradually get detrapped and cause some undesirable effects broadly called hydrogen embrittlement.

Formation of vacancy-hydrogen complexes has additional implications for plasma-wall interaction in fusion reactors. Thus, Myers *et al.*⁽¹⁾ performed a series of implantation-annealing experiments on various metals and determined binding energies of hydrogen (deuterium) with implantation-induced defects. In the case of Fe, they observed three annealing stages for implanted D at low temperatures, centering around 220, 260 and 350–450 K, with binding energies of 41, 61 and 69 kJ/mol, and assigned them, respectively, to detrapping from vacancies with 3–6 D's, vacancies with 1–2 D's, and small voids⁽²⁾. Multiple trapping of hydrogen atoms (up to 6 per vacancy) deduced from their series of work, was found to occur in this case as well.

A different approach to the vacancy-hydrogen interaction was started when we discovered the formation of extremely high concentrations of vacancies in metals heated under high hydrogen pressures—a phenomenon which we call the superabundant vacancy formation. This phenomenon, first discovered in Ni and Pd⁽³⁾⁽⁴⁾, was subsequently observed in other fcc and bcc metals as well (TiH₂⁽⁵⁾, Pd–Rh alloy⁽⁶⁾, Al⁽⁷⁾, Mo⁽⁸⁾), and is now believed to be quite general. We proposed⁽⁸⁾⁽⁹⁾ that the dominant mechanism of this effect is the lowering of the formation

energy of a vacancy by trapping hydrogen atoms in its neighborhood: the formation energy should be lowered by the sum of binding energies of trapped hydrogen atoms. An additional mechanism, the entropy effect, should also operate at high hydrogen concentrations: in order to recover the loss in the configurational entropy as the interstitial sublattice is filled up with hydrogen atoms, extra sites should be created on the metal sublattice. A statistical-mechanical theory based on these considerations has succeeded in giving a quantitative account of the vacancy concentrations observed in Ni and Mo⁽⁸⁾.

The purpose of this paper is to examine the formation of superabundant vacancies in Fe formed at high temperatures and high hydrogen pressures by measuring thermal desorption spectra of hydrogen atoms which remain trapped in the recovered samples. An advantage of this method of hydrogen charging over the commonly adopted method of cathode electrolysis is that it can be performed under well-defined equilibrium conditions, without causing any such damage as blisters, voids and/or plastic deformation.

II. Experimental Method

Samples were prepared from a 0.25 mm thick iron sheet of 99.99% in purity, purchased from Johnson-Matthey & Co. The residual resistivity ratio measured under a magnetic field of 0.1 T was 103, and contents of non-gaseous impurities determined by the supplier are given in **Table 1**.

Samples were heat-treated at prescribed temperatures (470–870 K) for 2 h under a hydrogen pressure of 1.7 GPa, recovered to ambient conditions, and then analyzed for remaining hydrogen by thermal desorption measurements.

The heat treatment under high hydrogen pressure was performed using a cubic-anvil press 'Oz.F2' of our laboratory. The design of a sample-cell assembly is

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Table 1 Impurity contents of the samples (Chemical analysis data supplied by Johnson-Matthey Company; in mass ppm)*

Co(23), Si, Ni(17), Mn(15), P(6.5), Cr(6.2), S(3.8), Ge(3.7), B(3.1), Na(1.3), Cu(1.2), K(0.5), Ca(0.3), Al, Mo(0.28), Zn(1.4), Cl(0.1), Nb, Ta(<0.1), V, W(0.09), Mg, As, Ti(0.07), Se, Sn, Cd(<0.05), Ba(0.02), F, Br, Pd, Sb, Te, I(<0.01), Be, Ga, Hf, Re, Os, Rb, Sr, Zr, Ru, Ag (<0.005), Li, Sc, Y, Rh, In, Cs, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy(<0.001).

*Notice; C, N, O are not included.

shown in **Fig. 1**. A sample ($\phi 2 \text{ mm} \times 0.2 \text{ mm}$) sandwiched between pellets of internal hydrogen source was enclosed in an NaCl capsule, surrounded by a graphite tube heater and a solid pressure transmitting medium (pyrophyllite). An internal hydrogen source adopted is a mixture of $\text{NaBH}_4 + \text{Ca}(\text{OH})_2$, which generates hydrogen by chemical reaction when heated to $\sim 570 \text{ K}$. Boron nitride separators serve as a sieve to block the passage of other reaction products. With this design, no contamination of samples was detected by plasma-emission analysis, even after more severe heat treatments (at $\sim 1270 \text{ K}$ for 5 h under 5 GPa of hydrogen pressure). After the runs, the sample and separators easily came apart, and the sample surface appeared as shiny metallic as before, except the case of 870 K heat treatment when the surface became slightly greyish. At 1.7 GPa, generated hydrogen was perfectly contained in the cell up to 970 K (A leakage started above this temperature.). The cell was compressed from all six sides equally by 6 mm $\times$ 6 mm tungsten carbide anvils to produce nearly homogeneous pressure at the center. The actual pressure generated was calibrated separately by resistance measurements of pressure-fixed points.

Thermal desorption spectra were measured using a simple vacuum system, with a quartz sample tube surrounded by a small furnace. After sample setting and evacuation to about 10^{-2} Pa (in 15 min), the system was

closed and its total pressure was measured subsequently during heating of the sample at a rate of 10 K/min. In order to improve the reproducibility, it was found necessary to start thermal desorption measurements at nearly the same time after recovery ($\sim 30 \text{ min}$ from the end of heat treatment to the beginning of temperature ramping for desorption measurements, a minimum time necessary for sample transfer). The reason for this will be discussed later.

After measuring the desorption spectra at several different holding times at two different temperatures (570 K in the α phase and 820 K in the γ phase region), the holding time of 2–3 h was judged to be sufficient for achieving thermal equilibrium states.

The temperature of phase transition $\alpha(\text{bcc}) \rightarrow \gamma(\text{fcc})$ under 1.7 GPa of hydrogen pressure was determined by *in situ* X-ray diffraction, using a similar cubic-anvil press MAX90 installed at the Photon Factory of KEK (Tsukuba). The cell design was very similar, the only difference being the use of amorphous boron powder cemented with epoxy resin as a pressure-transmitting medium.

III. Experimental Results

Let us begin with a brief description of the results of X-ray diffraction measurements under 1.7 GPa of hydrogen pressure. A gradual transition from $\alpha(\text{bcc})$ to $\gamma(\text{fcc})$ phase started at $\sim 770 \text{ K}$, and the two phases coexisted up to 870 K. Thus the α - γ phase boundary is drastically lowered by hydrogenation, in agreement with earlier observations^{(10)–(12)}. A small fraction (less than 1%) of the γ phase was retained after recovery to ambient conditions.

Thermal desorption data obtained after heat treatments at seven different temperatures are shown in **Fig. 2**. The results show that there are several desorption stages, and the total amount of desorbed hydrogen, x , increases with increasing temperature.

In order to see more clearly the desorption stages, the thermal desorption rate $-dx/dT$ was calculated by numerical differentiation, with the result shown in **Fig. 3**. We may identify five desorption stages, which we label A–E in the order of increasing temperature. The stages A and B, located at 400–440 K and 470–510 K, respectively, show up at holding temperatures $\geq 570 \text{ K}$, and increase in magnitude with increasing temperature. The extremely sharp desorption stage at 670 K, the stage D,

Fig. 1 Sample-cell assembly used for high hydrogen-pressure experiments. 1. sample (Fe), 2. hydrogen source ($\text{NaBH}_4 + \text{Ca}(\text{OH})_2$), 3. sample chamber (NaCl), 4. separator (BN), 5. electrode (Au), 6. tube heater (graphite), 7. thermocouple (C-A), 8. pressure transmitting medium (pyrophyllite).

Fig. 2 Amount of hydrogen desorbed after heat-treatments at seven different temperatures T_h for 2–3 h in 1.7 GPa of hydrogen pressure. Ramping speed is 10 K/min.

appears with varying magnitudes from run to run for holding temperatures higher than 770 K. The stages C and E, located at 500–540 K and 710–770 K, respectively, are seen clearly at low holding temperatures and appear to persist up to higher holding temperatures with nearly the same magnitude.

Before discussing the origin of these desorption stages, it will be appropriate to add some comments on the limitations of the method adopted here. First, the sample cell must be heated above ~ 570 K to generate hydrogen. This makes the 470 K data less reliable than the rest, because the cell had been heated to 570 K for 5 min before the holding at 470 K was started. Second, the limitation due to instability of the samples at room temperature. The stability of the samples after recovery to ambient conditions was examined by measuring desorption spectra at different starting times after the heat treatment: 0.5, 4.7, 21.5 and 139.5 h after holding at 770 K for 2 h. As shown in Fig. 4, the stage A disappeared completely after 139.5 h, whereas the stage B+C remained at $\sim 1/3$ of its original magnitude. Thus samples are not very stable under ambient conditions. Although the decay process cannot be described by a simple time law, the loss of stage A hydrogen before the desorption measurements may be roughly estimated to be 30%. This partial loss of hydrogen will have inevitable effects on the reproducibility of thermal desorption measurements.

IV. Discussions

A major objective of the discussion is to identify the state of hydrogen responsible for each desorption stage.

The simplest one appears to be the sharp stage D. This is believed to be due to the decomposition of the remnant γ phase, which contains fairly high concentrations of hydrogen. The fact that this stage appears only after heat treatments in the $\alpha + \gamma$ region, with varying magnitudes from run to run, supports this identification. As this stage is of minor importance for our present purpose, it will not be discussed further.

In order to help sorting out the rest of the stages, the total amount of desorbed hydrogen is plotted against the holding temperature in Fig. 5. There is a clear break in the slope at ~ 670 K: A process occurring at higher temperatures has the activation energy of ~ 100 kJ/mol, whereas at lower temperatures the process is nearly temperature-independent. Comparison with Fig. 3 shows that the stages A and B correspond to the higher-temperature process, and the stages C and E to the lower-temperature process.

The origin of the stages C and E is believed to be the detrapping from built-in lattice defects. Further discussions on their origin will be deferred to the end of this section.

Of the remaining stages A and B, the temperature dependence of their magnitudes suggests that the appearance of the stage B is correlated with the occurrence of the γ phase. Most of the γ phase was transformed to the α phase in the process of recovery (leaving only a small fraction as the remnant γ phase), and hydrogen atoms trapped in the γ phase during the heat treatments were retained in the α phase after the phase transformation. It must be admitted, however, that the mechanism of how the trapped state of hydrogen in the original phase can be retained after the transformation is not clear. In addition, the temperature range for the appearance of the stage B is rather limited. Thus we avoid these complications with the stage B and focus our attention on the stage A which arises after heat treatments in the α phase region.

It will be shown below that the stage A can be ascribed to the desorption of hydrogen released from vacancy-hydrogen complexes. In Fig. 6, amounts of hydrogen desorbed in the stage A are plotted against the holding temperature, including those of the stages A+B for comparison. The data points for the stage A, excluding the highest-temperature point, are well expressed by $x_{\text{des}} = 2.0 \times 10^4 e^{-(98 \pm 10) \text{ kJ} \cdot \text{mol}^{-1} / RT}$, as well as those of stage A+B up to the highest temperature (All the concentrations are expressed as ratios to the number of metal atoms.). Including the correction for the partial loss of hydrogen before the measurements, we obtain

$$x_{\text{des}} = 3 \times 10^4 e^{-(98 \pm 10) \text{ kJ} \cdot \text{mol}^{-1} / RT}. \quad (1)$$

Let us now examine this result in the light of our recent theory of superabundant vacancy formation⁽⁸⁾. The theory gives the thermal-equilibrium concentration of vacancy-hydrogen complexes x_v in the form

$$\frac{x_v}{1+x_v} = \frac{x_{i0}^{r_m}}{1-x_{i0}} \left(\frac{r_m}{r} \right)^{r_m} e^{-(g_v - r_m g_b) / RT}, \quad (2)$$

Fig. 3 The rate of desorption of hydrogen $-dx/dT$ obtained by numerical differentiation of Fig. 2.

$$\frac{r_m}{r} = 1 + \frac{1-x_{i0}}{x_{i0}} e^{-g_b/RT}. \quad (3)$$

In these expressions, x_{i0} is the probability of occupation of interstitial sites,

$$x_{i0} = \frac{x_H - r x_v}{x_{\max} - (r_m - 1) x_v}, \quad (4)$$

where x_H is the total hydrogen concentration, $x_{\max}$ is the total number of interstitial sites, r_m is the number of trapping sites per vacancy, and r the average number of trapped hydrogen atoms per vacancy. $g_f = h_f - s_f T$ is the free energy of formation of a vacancy in a pure metal, and $g_b = h_b - s_b T$ the binding free energy of a hydrogen atom to a vacancy. The total number of trapped (and subsequently desorbed) hydrogen atoms is then given by

Fig. 4 Checking runs to test the stability of hydrogens retained after recovery from high-pressure, high-temperature heat treatments (1.7 GPa, 770 K, 2 h). Amounts of hydrogen desorbed in stage A (400–440 K) and B + C (470–540 K) were measured at different times after recovery to ambient conditions.

Fig. 5 Arrhenius plot of the total amount of desorbed hydrogen against the temperature of heat treatments.

$$x_{\text{des}} = r x_v. \quad (5)$$

The solubility of hydrogen in α -Fe under a hydrogen pressure of 1.7 GPa is approximately given by

$$x_{\text{H}} = x_{\text{H}0} e^{-h_s/RT}, \quad (6)$$

with $x_{\text{H}0} = 1.6$ and $h_s = 28$ kJ/mol⁽¹³⁾. Thus $x_{i0} \ll 1$ holds at all temperatures of the present experiment ($x_{\text{H}} = 4.4 \times 10^{-3}$ at 570 K to 2.6×10^{-2} at 820 K, and $x_{\text{max}} = 1-3$). If, in addition, a condition

$$x_{i0} e^{g_b/RT} \gg 1 \quad (7)$$

holds, then r becomes nearly equal to r_m (complete trapping), and eq. (5) is reduced to

$$x_{\text{des}} = r_m e^{\Delta s_{\text{cl}}/R} e^{-h_{\text{cl}}/RT}, \quad (8)$$

$$\Delta s_{\text{cl}} = s_{\text{f}} - r_m s_{\text{b}} + R r_m \ln (x_{\text{H}0}/x_{\text{max}}), \quad (9)$$

Fig. 6 Arrhenius plot of the amounts of hydrogen desorbed in the stage A (filled circles) against the temperature of heat treatments. Those of the sum of stage A and B (open circles) are included for comparison.

$$h_{\text{cl}} = h_{\text{f}} - r_m h_{\text{b}} + r_m h_{\text{s}}. \quad (10)$$

Substituting $h_{\text{f}} = e_{\text{f}} + p v_{\text{f}} = 182 + 11 = 193 \pm 10$ kJ/mol⁽¹⁴⁾ and $r_m = 6$ into eq. (8), and comparing this with the experimental result, we obtain $h_{\text{b}} = 44 \pm 4$ kJ/mol and $\Delta s_{\text{cl}}/R = 8.5$. These values are consistent with the assumption of complete trapping: Substitution into eq. (3) gives $r/r_m = 0.984$ at 570 K and 0.965 at 820 K. The value of h_{b} agrees reasonably with the binding energies of Myers *et al.*: $e_{\text{b}} = 61$ kJ/mol for 1–2 H's and $e_{\text{b}} = 41$ kJ/mol for 3–6 H's around a vacancy⁽²⁾. The large value of Δs_{cl} is also reasonable in view of possible decrease of vibrational frequencies of trapped hydrogen atoms.

From the fact that the total amount of hydrogen atoms desorbed in the stages A and B is well represented by eq. (1), we may infer that all these hydrogen atoms were introduced in the same way by formation of vacancy-hydrogen clusters, subsequently transformed into two different states having different binding energies. Identification of these final configurations will not be made, however.

Let us compare these present results with other previous studies of trapped hydrogen in iron. Among numerous thermal desorption experiments reported, the work of Ono and Meshii⁽¹⁵⁾ dealt with high-purity specimens and introduced hydrogen by equilibration with 0.1 MPa of hydrogen gas at high temperatures (720 K and 1130 K). After quenching the specimens to 230 K, they measured thermal desorption spectra up to 800 K at ramping speeds of 1 and 2 K/min, and found two desorption stages around 220 K and 400 K. They examined the latter stage more closely, and found that after quenching from 1130 K and at a ramping speed of 1 K/min, the desorption peak temperature was 415 K and the concomitant binding energy was 49 ± 2 kJ/mol for polycrystals, and 395 K and 45 ± 2 kJ/mol for single

crystals. The corresponding trapping centers were assigned to be grain boundaries and dislocations, respectively. As the desorption stages in their experiment occurred at nearly the same temperature with nearly the same activation energy as the stage A of our experiment, it is tempting to re-assign their desorption stages to detrapping from vacancy-hydrogen complexes. However, this interpretation is not possible: The equilibrium hydrogen concentration in their experiment (8.5×10^{-5} at 1130 K) is too low to create vacancy-hydrogen complexes comparable to the observed trap concentrations (See eq. (2)).

More recently, Takai *et al.*⁽¹⁶⁾ investigated the thermal desorption of hydrogen charged by immersion of cold-drawn wires of high-purity iron in an NH_4SCN solution, and observed a broad peak extending from 370 to 570 K. A part of this peak was annealed out by holding at 473 K before the desorption measurements. They attributed this disappearing part to annihilation of vacancies and vacancy clusters, and the remaining part to detrapping from dislocations. Their results and interpretations are closely consistent with ours.

Finally, a brief discussion will be made on the origin of the desorption stages C and E. Judging from the amount of desorbed hydrogen in these stages, impurity atoms may appear to be the first candidate. The sum of impurity atoms given in Table 1 and other possible impurities C, N, O is comparable to the amount of desorbed hydrogen. However, consideration of binding energies points to the assignment otherwise. Comparison of desorption temperatures suggests that the binding energy for the stage C is only slightly higher than 60 kJ/mol, whereas that for the stage E should be much higher. On the other hand, reported binding energies of impurity atoms are generally lower than 60 kJ/mol; ~ 30 kJ/mol for substitutional impurities and 3–10 kJ/mol for interstitial impurities⁽¹⁷⁾. The defects having much larger binding energies (70–100 kJ/mol) are He bubbles created by implantation and the interfaces with some precipitate phases. Hydrogen atoms are supposed to be in the chemisorbed state on the internal surface of these defects. Thus our tentative assignment is that the stage C is due to detrapping from grain boundaries/dislocations, and the stage E to small bubbles formed in the process of recovery to ambient conditions.

Before closing the discussions, we wish to mention possible implications of the present results for hydrogen-embrittlement phenomena. The point is that hydrogen dissolution should be accompanied by vacancy formation until the vacancy concentration reaches the thermal-equilibrium value for that hydrogen concentration. From eq. (2), the expression at 300 K is derived as $x_v = 6.8 \times 10^{14} x_H^6$, which predicts rather high vacancy concentrations in regions where hydrogen is locally accumulated (e.g. near crack tips). The time necessary for the vacancy introduction is rather short due to a low migration energy of a vacancy in iron (53 kJ/mol⁽¹⁴⁾), amounting to only ~ 3 s for a diffusion distance of 1 μm . Thus, extra vacancies (vacancy-hydrogen clusters) will be

introduced continually in the crack-tip region, as the latter moves with the advancement of a crack. The presence of hydrogen-induced vacancies may be expected to be more effective than hydrogen itself in causing the "lattice decohesion" proposed by Oriani⁽¹⁸⁾ (In fact, the above expression for the vacancy concentration is valid for $6 \times 6.8 \times 10^{14} x_H^6 < x_H$, i.e. $x_H < 8 \times 10^{-4}$; above this concentration, some instability is expected to occur.). More serious efforts, both experimental and theoretical, must be made for clarifying the role of hydrogen-induced vacancies in hydrogen-embrittlement phenomena.

V. Conclusions

Of the five stages of hydrogen desorption from high-purity iron samples heat-treated under 1.7 GPa of hydrogen pressure, the one located at 400–440 K is identified as being due to the release from vacancy-hydrogen complexes, VacH_6 , the concentration of which amounts to 3×10^{-3} for 820 K holding. The binding energy of a vacancy is estimated to be 44 ± 4 kJ/mol.

Possible implications of the hydrogen-induced vacancies for crack-tip processes are pointed out.

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