Repulsive Nature for Hydrogen Incorporation to Fe₃C up to 14 GPa

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We have performed in situ X-ray diffraction measurements under high pressure and high temperature to study hydrogen solubility in Fe₃C carbide. Hydrogen solubility can be estimated from a volume expansion associated with hydrogen incorporation into metal. The lattice volumes and phase relations of Fe₃C–H system and Fe₃C were measured up to 14 GPa and 1973 K. The lattice volumes of Fe₃C measured in this study are well fitted using the 3rd order Birch–Murnaghan equation of state with the reported elastic parameters of Fe₃C. Obtained lattice volumes of Fe₃C–H are quite consistent with those of Fe₃C. No difference between the melting temperatures of Fe₃C–H and Fe₃C was observed. These results demonstrate that hydrogen incorporation into Fe₃C does not occur and hydrogen is unlikely to coexist with carbon in iron-alloy up to 14 GPa.

KEY WORDS: hydrogen solubility; iron carbide; high pressure.

1. Introduction

If hydrogen dissolves into metal or alloy, its melting temperature and physical properties are significantly changed. This hydrogen dissolution often causes hydrogen embrittlement. Although iron-carbide, Fe₃C, is widely used and closely related to steel-making process, hydrogenation of Fe₃C has never been studied systematically under pressure. Thus, it is important and required to clarify hydrogenation condition and hydrogen solubility in Fe₃C.

Hydrogenation reaction can be expressed as,

where M is metal and x represents hydrogen content in metal hydride (MH_x). If a system reach in chemical equilibrium of reaction (1) and chemical potential of hydrogen in MH_x (μ_s) is written as $\mu_s = 1/2\mu_f$ (μ_f is chemical potential of hydrogen gas), hydrogen content (x) can be expressed as follows,¹⁾

$$x = \frac{X}{\exp\left[\frac{h_s - 1/2\mu_f}{k_B T}\right] + 1} \quad \text{..... (2)}$$

where h_s , k_B , T , and X denote enthalpy of hydrogen in MH_x ,

Boltzmann constant, temperature, and maximum solubility of hydrogen in MH_x , respectively. Although μ_f is approximated by ideal gas equation ($\mu_f = \mu_0 + k_B T \ln P/P_0$) up to 0.1 GPa, μ_f starts to increase over the ideal gas behaviour above 0.1 GPa and to increase drastically above 1 GPa.^{2,3)} This leads effective hydrogen incorporation into metal or alloy under pressure.^{3,4)} For example, hydrogen incorporation into Fe₃⁵⁾ and Fe-10wt%Ni⁶⁾ are significantly promoted above 3 GPa. In case of iron-light element alloy, hydrogen solubilities into FeSi and FeS have been studied up to 19 GPa in previous studies.^{7,8)} Hydrogen tends to dissolve into FeSi above 10 GPa and into FeS above 3 GPa. The hydrogenation pressure of FeSi is much higher than those of Fe and FeS (~3 GPa). The hydrogen contents in FeSiH_x and FeSH_x are estimated to $x \sim 0.07$ – 0.22 and 0.2 – 0.4 , respectively. Those contents are clearly lower than hydrogen content in fcc and dhcp-FeH_x ($x \sim 1$). This suggests that hydrogenation pressure and hydrogen content strongly depend on the composition of iron-alloy. In this study, we have measured lattice volumes and phase relations of Fe₃C–H system and Fe₃C and estimated hydrogenation condition up to 14 GPa based on in situ X-ray diffraction (XRD) experiments under high pressure and high temperature.

2. Experimental

Starting material was Fe₃C powder (99.9% purity, Rare Metallic Co. Ltd.). Starting powder was identified as Fe₃C-

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cementite from X-ray diffraction pattern at ambient pressure and room temperature. The sample was enclosed in a cylindrical NaCl capsule, which was reported to seal hydrogen at high pressure.⁹⁾ LiAlH₄ was used as a hydrogen source and it was enclosed at the bottom of NaCl capsule. The Fe₃C sample and LiAlH₄ layers were separated by a thin MgO disc. After a thermal decomposition of LiAlH₄ at high temperature (423–493 K at ambient pressure),⁹⁾ H₂ was released and then supplied to the Fe₃C sample. Schematic picture of the cell assembly used are illustrated in **Fig. 1**.

High-pressure experiments were performed using 1 500 ton Kawai-type multi-anvil device (SPEED Mk-II) installed at BL04B1 beamline, SPring-8 synchrotron radiation facility.¹⁰⁾ High temperature was generated using cylindrical resistive heater made of graphite for the experiment below 7 GPa and of TiB₂–BN composite for the experiment above 7 GPa. Experimental temperature was monitored using a W3%Re–W25%Re thermocouple inserted in the heater. Experimental pressure was determined from lattice parameters of pressure markers (BN, MgO and NaCl) combined with their equations of state.^{11–13)}

In situ XRD measurement at high-pressure and high-temperature was carried out using white X-ray (vertical size: 0.2 mm × horizontal size: 0.1 mm) with an energy-dispersive method. XRD of the sample and the pressure markers were collected using Ge-solid state detector with a diffraction angle of 5.5°. X-ray diffraction of the sample at high temperature was collected with 100 K step from 300 K. To minimize the effect of sample grain growth on the diffraction patterns at high temperature, the press was oscillated from 0° to 4° during the XRD measurement.¹⁴⁾

To obtain hydrogen content in the sample using the lattice volume of the Fe₃C–H sample, we also need to know lattice volumes of Fe₃C at the present experimental conditions (see details in section 3.2). Thus, we also carried out separate experiments using Fe₃C sample and same cell assembly without hydrogen source (LiAlH₄) at the similar pressure and temperature conditions of Fe₃C–H sample. The experimental conditions are listed in **Tables 1** and **2**. The pressure and temperature conditions of this study ranges 5.3–15.3 GPa and 300–1 973 K, respectively.

Fig. 1. Schematic picture of the cell assembly used for the pressure above 7 GPa.

3. Results and Discussion

3.1. Phase Relations and Melting Temperatures of Fe₃C–H and Fe₃C

Typical XRD patterns of the Fe₃C–H sample are shown in **Fig. 2**. Based on XRD measurements, obtained phase relations of Fe₃C–H and Fe₃C are shown in **Fig. 3**. Difference in stable solid phase was not observed between Fe₃C–H and Fe₃C samples. In both cases, Fe₃C was confirmed to have an orthorhombic cementite structure (space group: *Pnma*) and there was no phase transition of Fe₃C in all the

Table 1. Experimental conditions and obtained lattice volume of Fe₃C–H system.

Run	P [GPa]	P error [GPa]	T [K]	Phases	V [Å ³]	V error [Å ³]	EOS V [Å ³]*
M807	6.79	0.02	673	Fe ₃ C	151.23	0.74	151.79
	6.64	0.14	773	Fe ₃ C	151.73	0.67	152.54
	6.50	0.02	873	Fe ₃ C	152.70	0.62	153.32
	6.35	0.25	973	Fe ₃ C	153.78	0.44	154.12
	6.21	0.25	1 073	Fe ₃ C	154.57	0.30	154.95
	6.06	0.25	1 173	Fe ₃ C	155.43	0.29	155.80
	5.91	0.25	1 273	Fe ₃ C	156.33	0.16	156.68
	5.76	0.25	1 373	Fe ₃ C	157.08	0.23	157.58
	5.61	0.25	1 473	Fe ₃ C	157.90	0.22	158.51
	5.45	0.10	1 573	Fe ₃ C	158.80	0.15	159.47
	5.28	0.08	1 673	Fe ₇ C ₃ +Liquid			
	5.28	0.08	1 703	Liquid			
M809	8.28	0.20	673	Fe ₃ C	149.73	1.04	150.74
	8.29	0.20	773	Fe ₃ C	150.50	0.82	151.36
	8.28	0.20	873	Fe ₃ C	151.18	0.83	152.01
	8.26	0.20	973	Fe ₃ C	152.24	0.35	152.69
	8.19	0.20	1 073	Fe ₃ C	153.08	0.30	153.43
	8.07	0.20	1 173	Fe ₃ C	153.96	0.26	154.22
	7.93	0.20	1 273	Fe ₃ C	154.79	0.20	155.05
M829	15.27	0.02	673	Fe ₃ C	144.20	1.92	146.30
	14.90	0.05	773	Fe ₃ C	145.78	0.38	147.07
	14.37	0.02	873	Fe ₃ C	147.14	1.02	147.97
	13.96	0.10	973	Fe ₃ C	148.12	0.71	148.82
	13.69	0.10	1 073	Fe ₃ C	149.36	0.60	149.61
	13.61	0.10	1 173	Fe ₃ C	150.25	0.22	150.29
	14.19	0.02	1 273	Fe ₃ C	150.97	0.08	150.56
	13.86	0.02	1 373	Fe ₃ C	151.93	0.09	151.44
	13.14	0.02	1 473	Fe ₃ C	152.79	0.17	152.63
	13.09	0.05	1 573	Fe ₃ C	153.79	0.13	153.37
	13.03	0.20	1 673	Fe ₇ C ₃ +Liquid			
	13.00	0.20	1 773	Fe ₇ C ₃ +Liquid			
	12.96	0.20	1 873	Fe ₇ C ₃ +Liquid			
	12.93	0.20	1 973	Liquid			

*EOS V represents the lattice volume of Fe₃C calculated using 3rd order Birch-Murnaghan EOS with reported elastic parameters.¹⁸⁾

Table 2. Experimental conditions and obtained lattice volume of Fe_3C .

Run	P [GPa]	P error [GPa]	T [K]	Phases	V [$\text{\AA}^3$]	V error [$\text{\AA}^3$]
M1049-1	7.14	0.02	573	Fe_3C	149.18	0.53
	7.01	0.02	673	Fe_3C	150.46	0.46
	7.12	0.02	773	Fe_3C	151.15	0.33
	7.19	0.02	873	Fe_3C	152.00	0.54
	7.15	0.20	973	Fe_3C	153.14	0.33
	7.14	0.20	1 073	Fe_3C	153.86	0.27
M1049-2	7.55	0.25	300	Fe_3C	149.30	0.35
	7.69	0.25	373	Fe_3C	149.35	0.32
	7.88	0.25	473	Fe_3C	149.77	0.33
	8.06	0.25	573	Fe_3C	150.21	0.31
	8.26	0.25	673	Fe_3C	150.68	0.30
	8.42	0.02	773	Fe_3C	151.15	0.31
	8.43	0.10	873	Fe_3C	151.70	0.29
	8.83	0.10	973	Fe_3C	152.36	0.29
	9.39	0.10	1 073	Fe_3C	153.00	0.26
	9.13	0.05	1 173	Fe_3C	153.73	0.22
	9.38	0.10	1 273	Fe_3C	154.49	0.19
	8.77	0.10	1 373	Fe_3C	155.26	0.09
	8.59	0.25	1 473	Fe_3C	156.25	0.09
	8.35	0.25	1 573	Fe_3C	157.07	0.08
	8.04	0.25	1 673	Fe_7C_3 +Liquid		
	7.82	0.25	1 773	Fe_7C_3 +Liquid		
	7.73	0.25	1 823	Liquid		
M831	14.90	0.02	673	Fe_3C	144.77	0.47
	14.71	0.02	773	Fe_3C	146.09	0.32
	14.47	0.02	873	Fe_3C	146.87	0.33
	14.00	0.02	973	Fe_3C	148.30	0.58
	14.35	0.02	1 073	Fe_3C	149.80	0.44
	14.08	0.05	1 173	Fe_3C	150.34	0.16
	13.69	0.05	1 273	Fe_3C	151.25	0.11
	13.34	0.05	1 373	Fe_3C	152.08	0.08
	13.01	0.25	1 473	Fe_3C	152.84	0.10
	12.37	0.25	1 573	Fe_3C	153.60	0.09
	12.36	0.25	1 673	Fe_7C_3 +Liquid		
	12.01	0.25	1 773	Fe_7C_3 +Liquid		
	11.69	0.50	1 873	Fe_7C_3 +Liquid		
	11.37	0.50	1 973	Liquid		

present pressure range before melting.

The sample melting was determined on the basis of disappearance of the sample diffraction peaks and appearance of diffuse scattering signal. It was confirmed that peak position of the diffuse scattering corresponded to the position where the most intensive sample peak was observed before melting. The Fe_3C melted incongruently to the liquid coexisted with Fe_7C_3 at 1 673 K, 5.3 GPa and at 1 673 K, 13 GPa

Fig. 2. XRD patterns of Fe_3C -H sample at 13 GPa and at 1 473 K (bottom), 1 773 K (top). At 1 473 K, most of the peaks were identified as Fe_3C cementite. Other peaks corresponded to NaCl and FeO as shown by “N” and asterisk, respectively. At 1 773 K, Fe_7C_3 coexisted with liquid.

Fig. 3. Phase diagram and melting curves of Fe_3C -H and Fe_3C samples. Circles and triangles represent Fe_3C -H and Fe_3C samples, respectively. White, gray and black symbols denote stability field of Fe_3C , Fe_7C_3 with liquid, and liquid, respectively. Black dashed-dotted curves show solidus and liquidus temperatures of Fe_3C -H sample. Solidus curve of the Fe_3C -H system corresponds to a tie line of temperatures between experimentally determined upper limit point where solid Fe_3C was observed and lower limit where Fe_7C_3 +liquid were observed. In the same manner, liquidus curve corresponds to the tie line of the temperatures between Fe_7C_3 +liquid and liquid. For reference, solidus and liquidus temperatures of Fe_3C ¹⁶⁾ are also plotted as thin gray dotted curves.

as shown in Fig. 2 (see also Table 1). Fe_7C_3 was a hexagonal structure as reported by Herbstein and Snyman.¹⁵⁾ This melting sequence is consistent with the result reported by

Nakajima *et al.*¹⁶⁾ Eutectic melting temperature (solidus) and liquidus curves of Fe₃C–H and Fe₃C are also drawn in Fig. 3. The solidus and liquidus temperatures of Fe₃C determined in this study are mostly consistent with those reported by Nakajima *et al.*¹⁶⁾ although the solidus of this study is slightly (~120 K) lower than that of Nakajima *et al.*¹⁶⁾ at 12.4 GPa. Our solidus and liquidus temperatures of Fe₃C–H sample agree well with those of Fe₃C in the pressure range studied. Hydrogen incorporation into metal often causes a depression of the melting temperature of the metal. For instance, in case of iron, the depression of melting temperature from Fe to FeH_x is reported to 600–900 K at 3–21 GPa.¹⁷⁾ Therefore, no difference in melting temperature between Fe₃C–H and Fe₃C is likely to reflect that hydrogen incorporation into Fe₃C does not occur at these pressures.

3.2. Lattice Volumes of Fe₃C–H and Fe₃C

In general, the lattice volumes of transition metals and alloys expand uniformly as a result of hydrogen incorporation into interstitial sites of metals and alloys.³⁾ The volume increase associated with hydrogen incorporation is, therefore, closely related to hydrogen content in the alloy. The hydrogen content (*x*) in metal hydride can be denoted by a following Eq. (3),

$$x = \frac{V_{MH_x} - V_M}{V_H} \dots\dots\dots (3)$$

where V_{MH_x} , V_M , and V_H represent atomic volumes of metal hydride and metal, and volume increase per hydrogen atom, respectively.³⁾ Thus, $(V_{MH_x} - V_M)$ indicates the volume increase caused by hydrogen incorporation. V_{MH_x} and V_M are directly obtained from the present diffraction measurements of Fe₃C–H and Fe₃C samples, respectively. Thus, the hydrogen content (*x*) can be calculated using Eq. (3) if the V_H is given.

Based on the XRD patterns, obtained lattice volumes of both Fe₃C–H and Fe₃C samples in the stability field of Fe₃C cementite phase are summarized in Tables 1 and 2, respectively. Change in the lattice volumes of Fe₃C–H and Fe₃C samples with temperature are shown in Figs. 4(a)–4(d). The lattice volumes of Fe₃C calculated using recently reported elastic properties of Fe₃C¹⁸⁾ with 3rd order Birch–Murnaghan equation of state were also shown in Fig. 4 by dotted curves. The lattice volume of Fe₃C–H sample increases with increasing temperature due to thermal expansion as observed in Fe₃C sample. The measured lattice volumes of Fe₃C–H and Fe₃C samples have relatively large errors below 873 K and slightly deviate from calculated volume of Fe₃C (dotted curves). However, measured volumes become to be consistent with calculated value above 873 K as shown in Fig. 4. This is because deviatoric stress is likely to remain still in the sample at temperatures below 873 K, which is supported by occurrence of XRD peak sharpening above

Fig. 4. The effect of temperature on the lattice volumes of Fe₃C–H (a, b) and Fe₃C (c, d) samples at around 8 and 14 GPa. Solid circles and triangles represent the volumes of Fe₃C–H and Fe₃C samples, respectively. Dotted curve indicate the calculated volume of Fe₃C using Birch–Murnaghan EOS and elastic parameters reported by Litasov *et al.*¹⁸⁾

873 K. After release of deviatoric stress above 873 K, it is found that there is no difference between the measured and calculated volumes. On the contrary, the Fe_3C sample for the measurement at 7.6–9.4 GPa was once heated up to 1 073 K before the XRD measurement at high temperatures. In this case, since the deviatoric stress was released by the primary heating, the measured lattice volume completely overlaps with calculated volumes even from 300 K (Fig. 4(c)).

The effect of pressure on the lattice volumes of $\text{Fe}_3\text{C-H}$ and Fe_3C samples at 1 073–1 473 K are shown in Figs. 5(a), 5(b). Obtained lattice volumes of Fe_3C match well with calculated compression curve of $\text{Fe}_3\text{C}^{18)}$ (Fig. 5(b)). The elastic properties used to calculate the compression curve are a lattice volume at ambient pressure $V_0=154.56 \text{ \AA}^3$, isothermal bulk modulus at ambient pressure $K_{0T}=190 \text{ GPa}$ and its pressure derivative $dK_T/dP=4.8$. Thermal contributions used are a temperature derivative of K_T ($dK_T/dT=-0.029 \text{ GPa/K}$

and thermal expansion $\alpha=(3.90\times 10^{-5})+(1.22\times 10^{-8})T \text{ K}^{-1}$. Thus, the lattice volumes of Fe_3C in this study are confirmed to agree with those of previous study.¹⁸⁾

The lattice volumes of $\text{Fe}_3\text{C-H}$ are in good agreement with those of Fe_3C in the range of present measurement up to 14–15 GPa as shown in Fig. 5(a). The lattice volumes of Fe_3C were calculated using the elastic properties of $\text{Fe}_3\text{C}^{18)}$ at the same P–T conditions of the experiments of $\text{Fe}_3\text{C-H}$ sample. Therefore, there is no difference in the lattice volumes between $\text{Fe}_3\text{C-H}$ and Fe_3C samples, i.e., $(V_{\text{MHx}}-V_M)\sim 0$. This result provides an important aspect that hydrogen incorporation associated with volume expansion does not occur to Fe_3C up to 14 GPa. This result is supported by no difference in solidus and liquidus temperatures between $\text{Fe}_3\text{C-H}$ and Fe_3C in the pressure range studied here.

In this study, hydrogen is supplied to Fe_3C from hydrogen source, LiAlH_4 , as a result of thermal decomposition of LiAlH_4 . The decomposition temperature of LiAlH_4 has been estimated to 423–493 K at ambient pressure, 573 K at 4.7 GPa, 873 K at 12 GPa, and 973 K at 18.5 GPa based on the hydrogenation temperature of iron-alloys in previous studies.^{9,7,17)} According to these results, most of the temperature conditions in this study are well above the decomposition temperature, suggesting that hydrogen was supplied to Fe_3C sample at the present conditions (only except for the conditions below 873 K at 14 GPa).

3.3. Stability of Carbide vs Hydride at High Pressure

The present results show that hydrogen does not react with Fe_3C up to 14 GPa. In terms of possible coexistence of hydrogen and carbon in iron, a reaction between Fe and $\text{C}_n\text{H}_{2n+2}$ (paraffin) has been studied recently based on a XRD measurement using a diamond anvil cell.¹⁹⁾ They reported that some chemical reactions were promoted at elevated temperatures and at 54 GPa. First, iron reacted with $\text{C}_n\text{H}_{2n+2}$ and Fe_3C carbide was formed with release of H_2 at 1 400 K (reaction [i]: $3n\text{Fe} + \text{C}_n\text{H}_{2n+2} = n\text{Fe}_3\text{C} + (n+1)\text{H}_2$), suggesting that H_2 coexists with Fe_3C as different isolated phases rather than forming hydride or H_2 in Fe_3C crystal structure. Then, at higher temperature (1 650 K), H_2 became to react with Fe_3C and FeH iron-hydride was formed together with diamond (reaction [ii]: $2\text{Fe}_3\text{C} + 3\text{H}_2 = 6\text{FeH} + 2\text{C}$). This result suggests that hydrogen does not coexist with carbon in iron-alloy. In other words, both hydrogen and carbon does not incorporate together into Fe. If carbon reacts with iron and Fe_3C is formed, H_2 exists as a different phase (reaction [i]). Alternatively, if hydrogen incorporates into Fe and iron-hydride is formed, then carbon exists as a different phase, such as diamond (reaction [ii]). In this study, stable coexistence of Fe_3C with H_2 (right hand side of reaction [i]) is confirmed in all the present temperature conditions up to 14 GPa. Therefore, hydrogen is not incorporated into carbide and exists as a different phase (such as H_2) at any temperatures at least up to 14 GPa and below 1 650 K at 54 GPa. At higher pressure and temperature (e.g., 54 GPa and above 1 650 K), hydrogen becomes to dissolve in iron-carbide and, then, carbide decomposes to diamond and iron-hydride. It is note that all these results suggest that disaffinity nature of hydrogen with carbon, i.e., hydrogen is not incorporated into iron with carbon.

There are several possible reasons for this repulsive effect

Fig. 5. The effect of pressure on the lattice volumes of $\text{Fe}_3\text{C-H}$ (a) and Fe_3C (b) samples at 1 073, 1 273, and 1 473 K. Dotted curve indicates the calculated volume of Fe_3C using Birch–Murnaghan EOS and elastic parameters reported by Litasov *et al.*¹⁸⁾ at respective temperatures.

of hydrogen to Fe₃C. One is due to a size of available interstitial site for hydrogen in Fe₃C cementite. Interstitial tetrahedral site of Fe₃C structure is likely to be much smaller than that of Fe and FeSi. Small size of interstitial site and short distance between the interstitial sites tend to block hydrogen incorporation.²⁰⁾ The other possible reason is due to a small value of μ_f for the Fe₃C–H₂ reaction (see Eq. (2)). For future study, in situ neutron diffraction measurement under high pressure is needed to investigate possible hydrogen position in iron-alloy structures and to clarify mechanism of hydrogen incorporation in iron-alloys. In situ neutron diffraction measurement under high pressure is now possible using the multi-anvil high pressure device, which was recently installed at a beamline of the J-PARC neutron facility.²¹⁾

4. Conclusions

The lattice volumes and phase relations were studied for Fe₃C–H and Fe₃C based on in situ XRD measurement up to 14 GPa and 1973 K. Obtained lattice volumes of Fe₃C–H matches well with those of Fe₃C. There is no difference between the melting temperatures (solidus and liquidus temperatures) of Fe₃C–H and Fe₃C. These results suggest that hydrogen does not incorporate into Fe₃C at the conditions of this study. Combining with the previous study,¹⁹⁾ it is most likely that hydrogen does not coexist with carbon in iron-alloy.

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