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Diffusion of carbon in iron under magnetic fields

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This study was conducted with the aim of investigating the effect of magnetic fields on the carbon diffusion in pure iron. The Fe/Fe-0.87 mass% C diffusion couples prepared by explosive welding were annealed at temperatures from 850 to 1200 K without and with a uniform magnetic field up to 6 T and with a magnetic-field gradient of 45 T/m. We evaluated the carbon diffusivity in iron from the penetration profiles of carbon into iron measured by secondary ionization mass spectroscopy. The diffusivity of carbon in α-Fe decreased under a magnetic field, while it increased by twice under a magnetic-field gradient.

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I. INTRODUCTION

Extensive studies have found that a magnetic field exerts influences on many metallurgical phenomena related to the development of microstructures in materials, such as recrystallization,[1–4] grain growth,[5,6] texture formation,[6–10] and phase transformation.[11–16] A strategy for precisely controlling the microstructure of materials by application of a magnetic field has been proposed with the aim of achieving enhanced properties. This is recently known as electromagnetic processing of materials (EPM). Most development of the microstructure is dominated by diffusion. However, the nature of diffusion under a magnetic field has not yet been fully understood.

Youdelis *et al.* have reported in 1964 that the application of a 3-T magnetic-field retarded diffusion of Cu in Al.[17] On the other hand, Nakajima *et al.*, who used a 4-T magnetic field, did not find any magnetic-field effects on diffusion of Ni in Ti.[18] Pokoev *et al.* revealed that the diffusivity of ^{63}Ni in pure iron and in an Fe-1.94 at.% Si alloy increased under a magnetic field of 0.1 T (Refs. 19 and 20) but the diffusivity conversely decreased with increasing the magnetic-field strength up to 0.7 T. Mironov *et al.* investigated the effect of a magnetic field of 0.7 T on diffusion of Ni in pure Co, and discussed the magnetic-field effect observed from the point of view of magnetostriction.[21] Recently, Nakamichi *et al.* have found that the diffusion of carbon in γ-Fe was retarded under a 6-T magnetic field.[22] In contrast to carbon diffusion, the diffusion of titanium in γ-Fe was not affected by application of a magnetic field. They suggested that the magnetic-field effect on diffusion would change according to the mechanism of diffusion. Furthermore, they conducted the diffusion experiments under a magnetic-field gradient. The diffusivity of carbon was found to increase under a "negative" magnetic-field gradient, while decrease under a "positive" magnetic-field gradient. The sign of magnetic-field gradient was defined as negative when carbon atoms penetrate toward the higher magnetic-field direction. Ohtsuka *et al.* have investigated the effect of a uniform magnetic field on the formation of apearlite phase in a diffusion couple of Fe/Fe-0.8 mass% C.[23] They concluded that diffusion of carbon in γ-Fe was retarded by the application of a magnetic field, because the rate of pearlite phase transformation decreased under a magnetic field.

Recently, the diffusion under an ac magnetic field and a pulse magnetic field has been studied. Rabkin *et al.*, who used a thermal grooving technique, have reported that the surface diffusion of Fe decreased under an alternative magnetic field of 0.5 T (50 Hz).[24] Liu *et al.* have investigated the effect of an ac magnetic field of 0.5 T on the interdiffusion of Al/Zn and Al/Mg.[25,26] They estimated the diffusion coefficients from the growth rate of the intermediate phases, and found that the magnetic field increased the diffusivity. They pointed out that an increase of the diffusivities was owing to the change in the preexponential frequency factor but not in the activation energy by the application of a magnetic field. Verzhakovskaya *et al.* have investigated the effect of pulsed magnetic field on the diffusion of Al atoms in pure iron.[27,28] They found that the pulsed magnetic field increased the Al diffusion, and discussed the magnetic-field effect from the viewpoint of the interaction between magnetic domains and dislocations.

As mentioned above, many studies on the effect of a magnetic field on diffusion have been conducted so far. However, the results reported are not necessarily consistent with each other. One main motivation of this work is to determine diffusivity of carbon in iron, particularly in α-Fe, under a magnetic field and a magnetic-field gradient, because diffusion of carbon plays an important role for the development of microstructures in steel.

II. EXPERIMENTAL

A. Specimen preparation

Measurements of carbon diffusion in iron under a magnetic field and a field gradient were conducted with a diffusion couple of pure iron (99.9%) and eutectoid steel (Fe-0.87 mass% C).[29] The diffusion couples used in this study were prepared by an explosive welding method at the shock wave and condensed matter research center of Kumamoto University in order to prevent diffusion of carbon during joining. The plastic explosive (SEP), which consisted mainly of nitric ester, was used as an explosive. Before joining, plates of pure iron and eutectoid steel, which were 100 mm × 50 mm × 5 mm and 100 mm × 50 mm × 2 mm in size, respectively, were annealed at 973 K for 86.4 ks in a vacuum of 2 mPa. They were mechanically ground to remove the oxide scale. The specimens were cut from the explosively welded iron and steel clad into

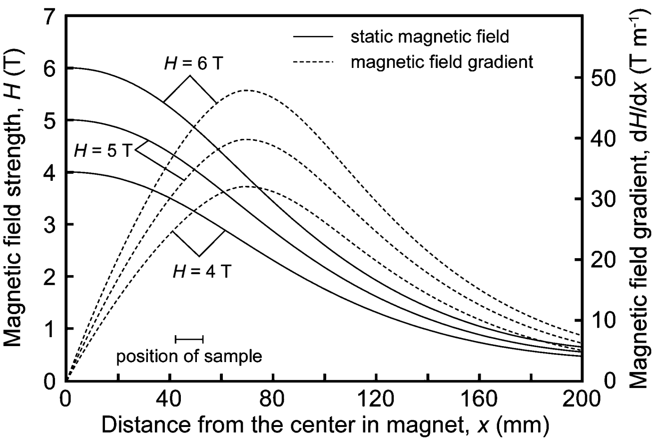

FIG. 1. Variation of a magnetic field H and a magnetic field gradient dH/dx with the position x in the magnet for different nominal magnetic fields H_0.

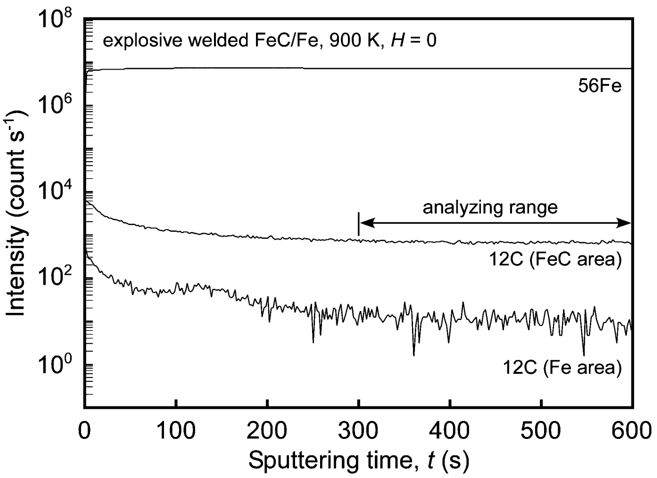

FIG. 2. An example of SIMS profiles for ^{56}Fe and ^{12}C in steel and iron.

a plate of 7 mm × 5 mm × 1 mm in dimension. Thereafter, they were mechanically polished with waterproof papers of #320–#2000 and buff polished with alumina particles of 3 and 1 μm.

B. Diffusion annealing under a magnetic field and a magnetic-field gradient

The superconducting magnet equipped with an electric furnace using a Mo sheet heater was used in this study. This magnet was HF6-100VHT-1, with a bore size of 100 mm in diameter, from Sumitomo Heavy Industries, Ltd. The maximum magnetic field and temperature obtained with this system were 6 T and 1773 K, respectively. For diffusion annealing with this system, we used a specially designed carbon sample holder. A sample was sandwiched by tungsten sheets to prevent carbon contamination and they were inserted into the carbon holder. The annealing for diffusion was conducted at temperatures from 850 K [below Curie temperature (1043 K)] to 1200 K [above α-γ phase transformation temperature (1184 K)] in a vacuum of 1.0×10^{-3} Pa. The annealing time was determined so that carbon atoms could penetrate into pure iron by ~800 μm on the basis of previous data.[30,31] The applied magnetic-field strength was 0–6 T and applied magnetic-field gradient was 45 T/m [$H\,(dH/dx) = 2.08 \times 10^2$ T^2/m]. A magnetic-field gradient was applied by placing the samples apart from a uniform magnetic-field region. Figure 1 shows the variation of magnetic-field strength H and magnetic-field gradient $-dH/dx$ along the position from the center of the magnet. The direction of the applied magnetic field was perpendicular to the iron and steel interface, which was parallel to the diffusion direction. Because the magnetic field was applied to the longitudinal direction of the plate specimens, the demagnetization field was assumed to be negligible. Details of the annealing conditions for carbon diffusion in pure iron under a magnetic field are shown in Table I.

C. Evaluation of diffusion coefficients

The carbon penetration profiles from the iron and steel interface to iron were measured by secondary ionization mass spectroscopy (SIMS; Atomika Ion Microprobe 4100). The primary ion beam used in this study was O^{2+} ion at an energy of 5.00 keV, and could be converged to a diameter of less than 100 μm. Figure 2 shows an example of ^{57}Fe and ^{12}C SIMS profiles obtained from the areas in the eutectoid steel and the pure iron. The carbon concentration from the detected counts of the SIMS analysis was evaluated as a function of the distance from the interface. The distances were measured from the traces sputtered by an ionic beam during the SIMS analysis. Because the SIMS counts approached a constant

TABLE I. Annealing conditions for Fe and steel specimens.

Temperature, T (K)	Annealing time, t (ks)	Magnetic field: Uniform field, H (T)	Magnetic field: Field gradient, dH/dx (T/m)
850	133	0, 6	45
900	30.5	0, 6	–
950	15.4	0, 6	45
1000	8.34	0, 2, 4, 6	45
1050	4.79	0, 6	–
1100	2.89	0, 6	45
1150	1.82	0, 6	45
1200	41.2	0, 6	45

value by sputtering for 300 s, the counts for carbon was defined as the sum of the counts from 300 to 600 s. The carbon concentration was quantitatively estimated from the carbon counts obtained at a position normalized by the counts from the steel with a ready-known carbon concentration. To reduce the effect of grain-boundary diffusion on the estimation of carbon diffusivities, the carbon concentration was estimated only from grain-boundary-free regions. From these results, concentration profiles of carbon in iron were obtained. The diffusion coefficients of carbon in iron were determined according to Fick's second law, given by

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}, \tag{1}$$

where C is the concentration of atoms, t is the diffusion time, D is the diffusion coefficient, and x is the diffusion length.

III. RESULTS

A. Penetration profiles of carbon in pure iron

The carbon penetration profiles were measured from the iron and steel interface to the pure iron in the diffusion couples annealed without and with a magnetic field. Figure 3 represents optical micrographs showing traces sputtered by the ion beam of SIMS for the specimens annealed at 1000 K [Figs. 3(a) and 3(b), ferromagnetic α-Fe], 1100 K [Figs. 3(c) and 3(d), paramagnetic α-Fe], 1150 K [Figs. 3(e) and 3(f), paramagnetic α-Fe], and 1200 K [Figs. 3(g) and 3(h), paramagnetic γ-Fe] under nonmagnetic and a 6-T magnetic field. No cementite (Fe_3C) precipitates were observed even at the iron and steel interface, and grain boundaries and grain-boundary triple junctions in iron after the specimens were annealed below 1100 K [Figs. 3(a)–3(d)]. On the other hand, fine cementite precipitates and transformation strain were observed in iron near the interface in the specimen annealed at 1150 K [Figs. 3(e) and 3(f)]. This is probably because the α-γ phase transformation temperature locally decreased owing to the penetration of carbon into pure iron from the interface, and then phase transformation occurred in the vicinity of the interface of the diffusion couple. Carbon atoms solved in α-Fe at 1150 K precipitated as a cementite phase during cooling to room temperature. The ferrite and pearlite phases coexisted in the specimens annealed at 1200 K [Figs. 3(g) and 3(h)] .

Figure 4 shows the changes of carbon concentration in iron as a function of the distance from the interface between steel and iron at (a) 1200 K, (b) 1100 K, and (c) 1000 K under a nonmagnetic and a 6-T uniform magnetic field. The solid lines in Fig. 4 were fitted curves based on the error-function distribution [Fig. 4(a)] and on the Gaussian distribution of carbon concentrations [Figs. 4(a) and 4(c)], as described in the following section. Because of the phase transformation, the diffusion couple of eutectoid steel and pure iron consists of a pair of γ-Fe/γ-Fe phases, respectively, at 1200 K, γ-Fe/α-Fe at 1100 K, and a pearlite/α-Fe at 1000 K. The carbon concentration C_C in iron exponentially decreased with increasing penetration distance from the interface, irrespective of whether a magnetic field was applied. In addition, the carbon concentrations near the interface are higher in the specimens annealed under a magnetic field than under a nonmagnetic field, and the concentration gradient is larger under a magnetic field than under a nonmagnetic field. These results suggest that the solid solubility of carbon in iron increases and the diffusivity decreases by the application of a 6-T magnetic field.

B. Effect of a magnetic field on diffusivity of carbon in iron

The carbon diffusivities in iron under a nonmagnetic field and a magnetic field were measured from the carbon penetration profiles shown in Fig. 4. For the case of a pair of semi-infinite solids such as the diffusion couples used in this study, a solution to the diffusion equation is generally given by the error-function solution as shown by Eq. (2),

$$C_C(x,t) = C_0\left[1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right], \tag{2}$$

where erf stands for the error function, D is the carbon diffusion coefficient, t is the annealing time for diffusion, and x is the penetration distance of carbon in iron. From Eq. (2), the inverse error function of carbon concentration is proportional to diffusion distance as described in Eq. (3):

$$\operatorname{erf}^{-1}\left[1 - \frac{C_C(x,t)}{C_0}\right] = \frac{x}{2\sqrt{Dt}}. \tag{3}$$

Following Eq. (3), the values of $\operatorname{erf}^{-1}[1 - C_C(x,t)/C_0]$ were plotted against the penetration distance of carbon atoms as shown in Fig. 5(a). There are good linear relationships (correlation coefficients were 0.74–0.97) between them above 1100 K, irrespective of whether or not a magnetic field was applied. Accordingly, the diffusion coefficients were estimated from the slope of the straight lines in Fig. 5(a). On the other hand, when the temperature for diffusion annealing is below 1100 K, it is hard to consider that carbon atoms are infinitely supplied to the interface from a pearlite phase in eutectoid steel. Thus, we assumed that a thin-film layer of α-Fe in which carbon concentration is reached to the solid solubility limit of carbon in iron at a given temperature is formed at the beginning of diffusion annealing, and therefore that the distribution of carbon in iron after some diffusion would be that given by the thin-film solution. In addition, if the surrounding regions are initially solute free, the profile cannot be different from the Gaussian distribution observed in thin-film geometry at the beginning of diffusion annealing.[32] The solution of Fick's second law is represented by the following equation for the thin-film geometry:

$$C_C(x,t) = \frac{S_0}{\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right), \tag{4}$$

where S_0 is the number of atoms at the interface between the iron and steel per area, D is the carbon diffusion coefficient, t is the annealing time for diffusion, and x is the penetration distance of carbon in iron. Diffusion coefficients of carbon in α-Fe can be evaluated according to Eq. (4) when the relationship between the carbon concentration and the penetration distance is obtained as shown in Figs. 4(b) and 4(c). Following Eq. (4), the natural logarithm of C_C was plotted as a function of the square of the penetration distance as shown in Figs. 5(b) and 5(c). Good linear relationships between them

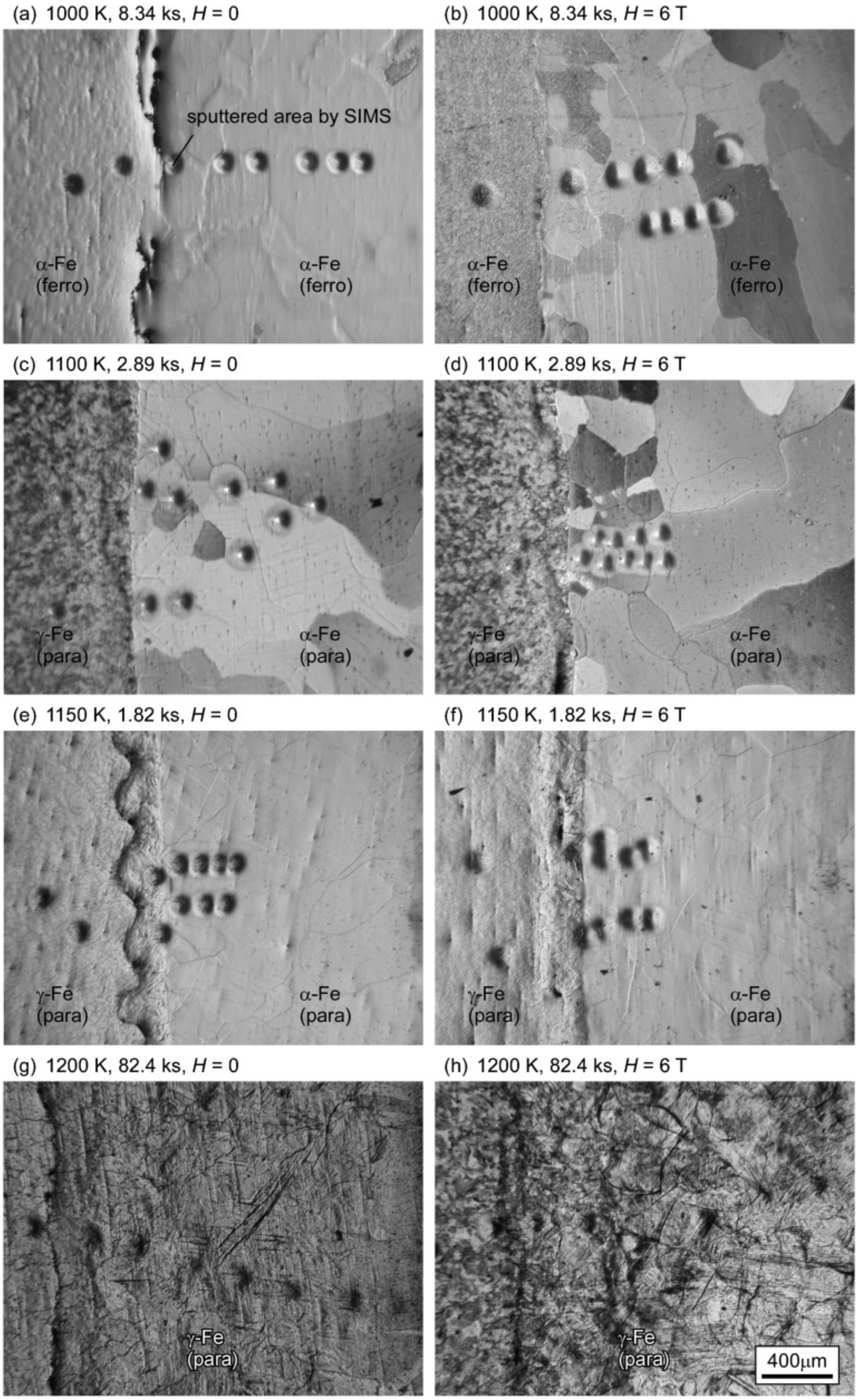

FIG. 3. Optical microscope images after SIMS analysis in iron and steel diffusion couples annealed at (a), (b) 1000 K (ferromagnetic α-Fe), (c), (d) 1100 K (paramagnetic α-Fe), (e), (f) 1150 K (paramagnetic α-Fe), and (g), (h) 1200 K (paramagnetic γ-Fe).

(correlation coefficients: 0.67–0.99) is obtained, irrespective of whether or not a magnetic field was applied. Furthermore, the diffusion coefficients of carbon below 1100 K estimated using Eq. (4) were more consistent with the previous data[31] than those estimated using Eq. (3). This finding indicates that the assumption made above is the case, and then Eq. (4) can be

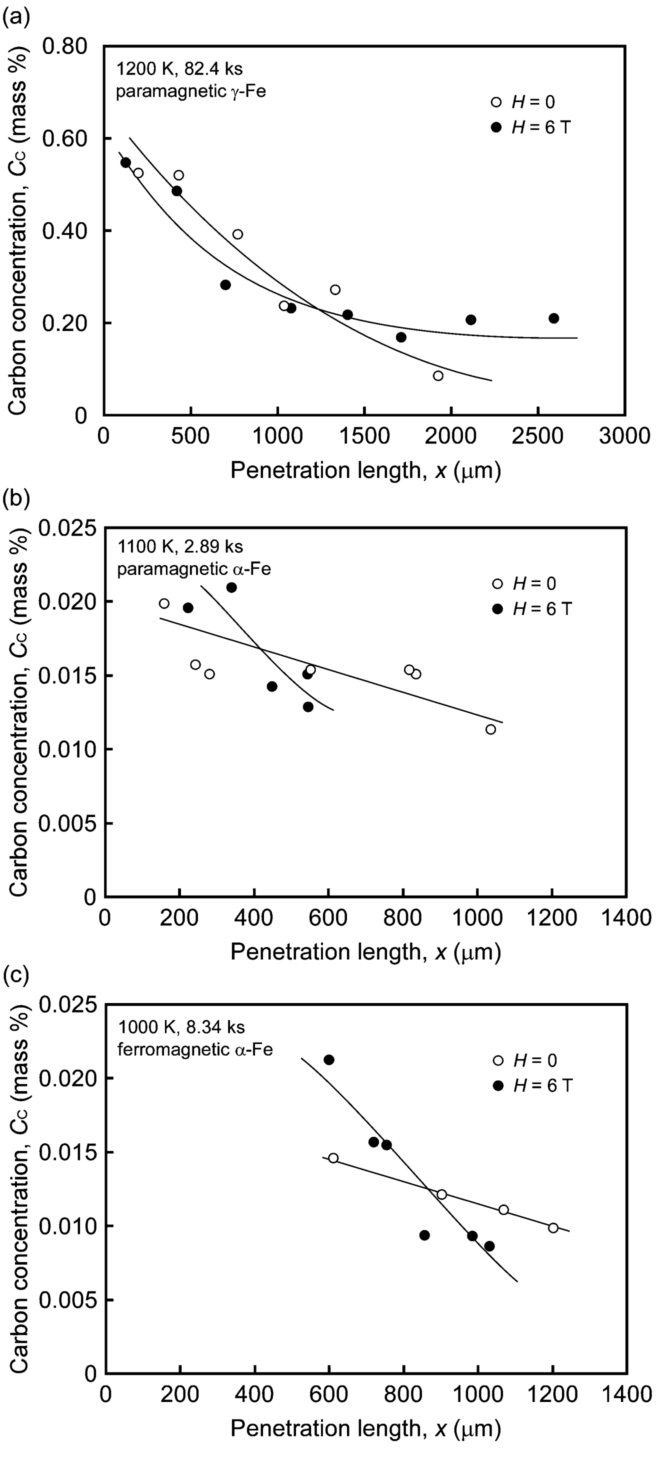

FIG. 4. Carbon concentration distributions in pure iron as a function of diffusion length in the iron and steel diffusion couples annealed at (a) 1200 K, (b) 1100 K, and (c) 1000 K without and with a 6-T magnetic field.

applied to the diffusion system used in this study to estimate the diffusion coefficients of carbon in iron below 1100 K.

The diffusion coefficients estimated at each temperature are summarized in Table II with the rate of diffusivity change owing to a 6-T magnetic field. The diffusion coefficients of carbon in iron were decreased by ∼67% at the ferromagnetic α-Fe temperature range, 69% at the paramagnetic α-Fe, and 38% (Ref. 22) at the paramagnetic γ-Fe when a 6-T magnetic field was applied. The difference between reduction rates of diffusion coefficients at ferromagnetic α-Fe and those at paramagnetic α-Fe were not significant, probably because of the occurrence of the magnetic-field-induced magnetization beyond the Curie temperature.[33] The diffusion coefficient estimated at 1100 K in paramagnetic α-Fe without a magnetic field was in good agreement with previous data.[31] Although a strain introduced by explosive welding to prepare the diffusion couple was reported to increase the diffusivity,[34] the significant effect of explosive welding on diffusivity was not observed in this study. The estimated carbon diffusion coefficient at 1150 K without a magnetic field would be lower, and that at 1200 K under a magnetic field would be higher than those expected. The reasons for these will be mentioned below.

Figure 6 shows the Arrhenius plots of diffusion coefficients of carbon in α-Fe and γ-Fe under nonmagnetic and 6-T magnetic fields. For comparison, the reported data,[22,30,31] which was obtained under a nonmagnetic field, are shown in Fig. 6 by the dashed lines. It is well known that the Arrhenius plots of carbon diffusivity exhibits a positive deviation from linearity with increasing temperature below the Curie temperature owing to the effect of magnetic spin ordering.[35] However, the approximate linear Arrhenius relationship is recognized in the temperature range shown in Fig. 6, irrespective of whether a magnetic field was applied. Thus, the activation energies for the carbon diffusion were calculated by the slopes of the straight lines in Fig. 6. Those under a nonmagnetic field and a 6-T magnetic field both were evaluated to be ∼117 ± 12 and 112 ± 12 kJ/mol, respectively. A magnetic field would not significantly affect the activation energy for carbon diffusion, so that it was difficult to explain the 70%–80% decrease in diffusion coefficient by a magnetic field from the viewpoint of activation energy. Therefore, we concluded that the magnetic field would exert an observable influence on the preexponential factor of carbon diffusion in α-Fe much more than the activation energy of that. It was reported so far that the magnetic field did not significantly affect the activation energy but it did affect the preexponential factor for some phenomena closely related to the diffusionlike grain growth under an applied magnetic field.[25,36]

The diffusion coefficient at 1150 K showed lower values than were expected from extrapolating the temperature dependence of diffusivity for under a nonmagnetic field, because the carbon penetration into α-Fe may have caused the transformation of α-Fe into γ-Fe, in which the carbon diffusivity is much lower than that in α-Fe, in the vicinity of the interface. In particular, the decrease in diffusivity was significant under a nonmagnetic field, implying that a magnetic field would increase the α-γ transformation temperature. The γ phase predominantly nucleates at the grain boundaries or triple junctions in the α-γ phase transformation. When carbon atoms segregate at the grain boundaries, nucleation of the γ phase at grain boundaries would be more pronounced. Tsurekawa *et al.* have reported that the grain-boundary segregation of Sn atoms in iron was suppressed by the application of a magnetic field.[37,38] If a magnetic field would decrease the grain-boundary segregation of carbon atoms in iron as well, the α-γ phase transformation would be

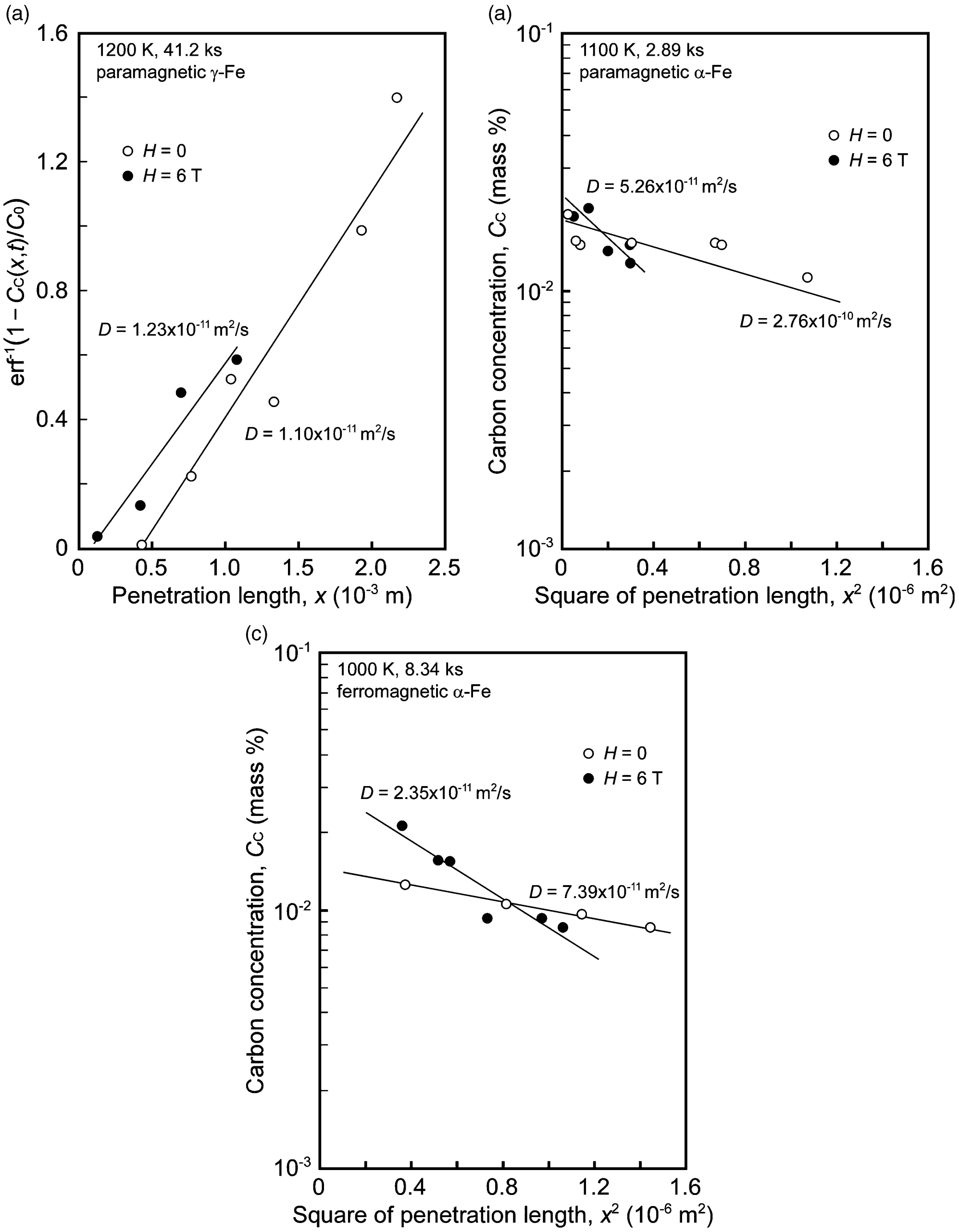

FIG. 5. The estimation of carbon diffusivities in the iron and steel diffusion couples annealed at (a) 1200 K, (b) 1100 K, and (c) 1000 K without and with a 6-T magnetic field.

delayed under a magnetic field. Moreover, there are some theoretical[39] and experimental[40,41] works reporting that the α-γ transformation temperature increased under a magnetic field. From these results, the decrease in carbon diffusivity under a magnetic field at 1150 K would not be observed such as that under a nonmagnetic field. Moreover, the diffusion coefficient obtained at 1200 K under a magnetic field was higher than that expected from the previously reported one,[22] whereas the coefficient under a nonmagnetic field was in good agreement with the previous one.[30] This finding suggests that the ferrite phase may have been still existing owing to an increase in the α-γ transformation temperature by a magnetic field.

Figure 7 shows the logarithm of carbon diffusivity at 1000 K as a function of the magnetic-field strength. The logarithm of the carbon diffusion coefficient in α-Fe is found to decrease linearly with increasing magnetic-field strength.

C. Effect of a magnetic-field gradient on diffusivity of carbon in iron

The carbon diffusivity in ferromagnetic α-Fe was investigated under a magnetic-field gradient of 45 T/m. Figure 8 shows the carbon concentration profiles as a function of the distance from the interface between steel and iron in the diffusion couple annealed at (a) 1000 K and (b) 950 K

TABLE II. Carbon diffusion coefficients in pure iron.

Temperature, T (K)	Diffusion coefficient, D (m^2/s) $H = 0$	$H = 6$ T	Rate of change
850	6.27×10^{-12}	2.16×10^{-12}	−65.5
900	1.15×10^{-11}	3.94×10^{-12}	−65.7
950	3.00×10^{-11}	9.12×10^{-12}	−69.6
1000	7.39×10^{-11}	2.35×10^{-11}	−68.2
1050	1.19×10^{-10}	4.30×10^{-11}	−63.7
1100	2.76×10^{-10}	6.93×10^{-11}	−74.9
1150	(1.83×10^{-10})	(2.05×10^{-10})	(12.0)
1200	(1.10×10^{-11})	(1.23×10^{-11})	(12.0)
1223[a]	1.3×10^{-11}	7.9×10^{-12}	−38.9
1273[a]	1.8×10^{-11}	1.1×10^{-11}	−47.4
1323[a]	3.8×10^{-11}	2.0×10^{-11}	−28.3

[a] Data from Nakamichi *et al.* (Ref. 22).

under a nonmagnetic field and a magnetic field gradient of 45 T/m. Following Nakamichi *et al.*,[22] the sign of a magnetic-field gradient is defined as negative when a flux of carbon atoms produced by a concentration gradient occurs toward a higher magnetic-field strength. When a negative magnetic-field gradient was applied, the carbon concentration in pure iron increased in comparison with the specimen annealed without a magnetic-field gradient. In addition, conversely to under a uniform magnetic field, the gradient of carbon concentration in iron under a magnetic-field gradient is smaller than that without a magnetic field. The relationships between the natural logarithm of C_C and the square of the penetration depth are shown in Fig. 9. There are good linear relationships between them, so that the carbon diffusion coefficients under a magnetic-field gradient were estimated from the slopes of the straight lines by Eq. (4). Figure 10 shows the Arrhenius plots of the measured diffusion coefficients of carbon under a negative magnetic-field gradient. For comparison, the diffusion coefficients without and with a uniform magnetic field are also shown. It was evident that the diffusion coefficients of carbon in iron were increased by ∼115% under a negative magnetic-field gradient. The activation energies for carbon diffusion in α-Fe were estimated to be 100 ± 13 kJ/mol. Taking into consideration the experimental error, no significant effect of a magnetic-field gradient on the activation energy was observed.

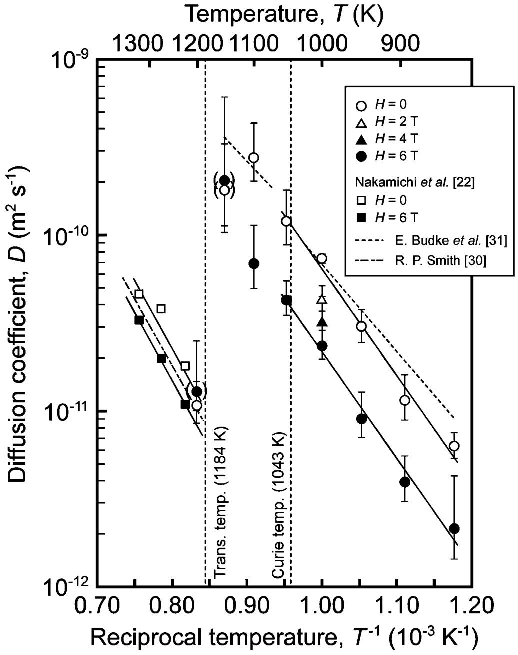

FIG. 6. Arrhenius plots of the carbon diffusion coefficients in pure iron under uniform magnetic fields of 2–6 T. For comparison, the reported data (Refs. 22, 30, and 31), which were obtained under nonmagnetic field, are shown by the squares and the dashed lines.

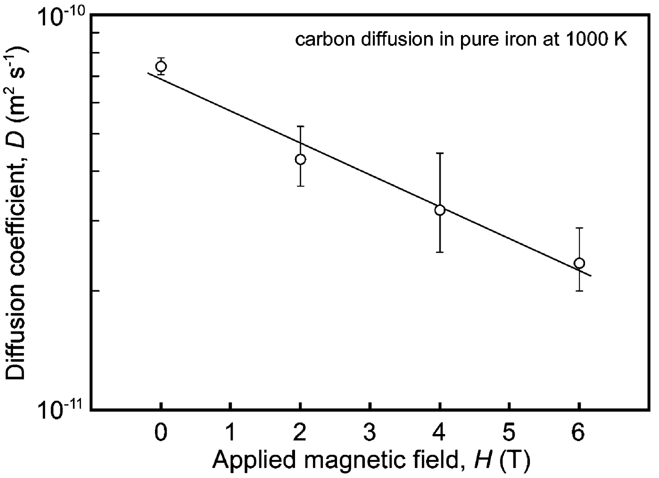

FIG. 7. The dependence of magnetic-field strength on the diffusion coefficient of carbon atoms in iron.

IV. DISCUSSION

A. Effect of a magnetic field on diffusivity of carbon in iron

The diffusivity of interstitial atoms such as carbon is described by

$$D = \frac{1}{n}\nu d^2 \exp\left(\frac{S_D}{R}\right)\exp\left(-\frac{H_D}{RT}\right), \tag{5}$$

where ν is the frequency of atoms, d is the jump length of carbon, H_D is the activation enthalpy of diffusion, S_D is the diffusion entropy, R is the gas constant, and T is the absolute temperature.[42] The enthalpy and entropy of diffusion are identical with the migration quantities of the interstitial. From the experimental results shown in Fig. 6, H_D in Eq. (5) is less dependent on an applied magnetic field. Although the jump length would slightly change along the magnetic-field direction owing to the magnetostriction,[43] a change in average jump length is assumed to be negligible because the jump length along each crystallographic direction in the iron lattice would be averaged out. In addition, we assumed that the frequency of atoms ν will not significantly change under a magnetic field. Consequently, a decrease in diffusivity under a magnetic field would be attributed to the diffusion entropy, and the diffusivity will exponentially decrease with decreasing the diffusion entropy. As shown in Fig. 7, the diffusivity was found to be exponentially decreased with increasing magnetic-field strength. Thus, the diffusion entropy should be a linear function of the magnetic-field strength. Therefore, it is concluded that

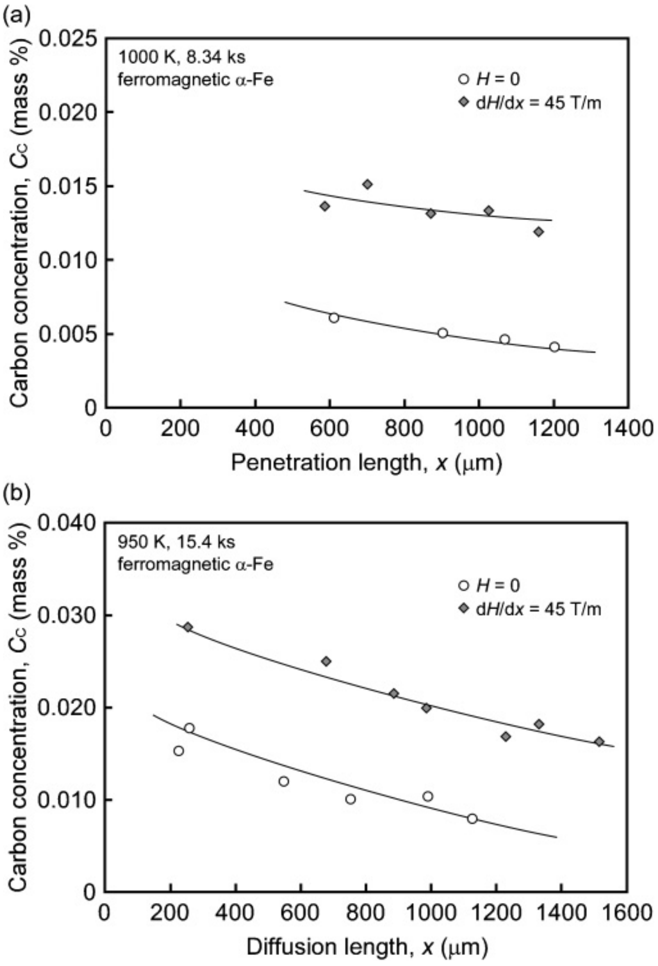

FIG. 8. Carbon concentration distributions in pure iron as a function of diffusion length in the iron and steel diffusion couples annealed at (a) 1200 K and (b) 1000 K without and with a 45 T/m magnetic-field gradient.

a decrease in the diffusion entropy owing to a magnetic field will be responsible for the decrease in the carbon diffusivity in the observed iron.

Here the activation entropy of carbon diffusion under a magnetic field was discussed from the viewpoint of site occupancy of carbon in iron. The carbon atoms in α-Fe are predominantly located in the octahedral sites of the bcc lattice. Thermodynamic calculations revealed that the percentage of the tetrahedral-site occupancy is not more than 0.1% in α-Fe.[44] A change in diffusion entropy of interstitials would be expected if some carbon atoms could rearrange from the octahedral sites to the tetrahedral sites because of changes in vibrational entropies for octahedral sites and for tetrahedral sites.[44] Thus, the fraction of solute atoms located at the octahedral sites can significantly affect the diffusion entropy. If a magnetic field could exert an influence on this fraction, the diffusivity of carbon would change. This may occur because of the magnetostriction. When a magnetic field is applied, a $\langle 100 \rangle$ direction is extended because of a positive value of the volume magnetostriction constant for the $\langle 100 \rangle$ directions in α-Fe.[43] Thus, the octahedral sites would be energetically more favorable for carbon atoms in α-Fe under a magnetic field. Because there is a large difference between the diffusivities of carbon at octahedral sites and at tetrahedral sites,[44] the application of a magnetic field is likely to change the diffusivity of carbon owing to the change in the fraction of carbon atoms at two distinct interstitial sites. This will be discussed further discussion in the next section on the basis of a dual-occupancy model.[44,45]

Carbon atoms in fcc γ-Fe are known to occupy only octahedral sites, unlike bcc α-Fe. Therefore, the configurational entropy of carbon atoms in γ-Fe would not change even if a uniform magnetic field is applied. The nearest-neighboring iron atoms for carbon at octahedral sites are located along the $\langle 100 \rangle$ directions in γ-Fe. However, the

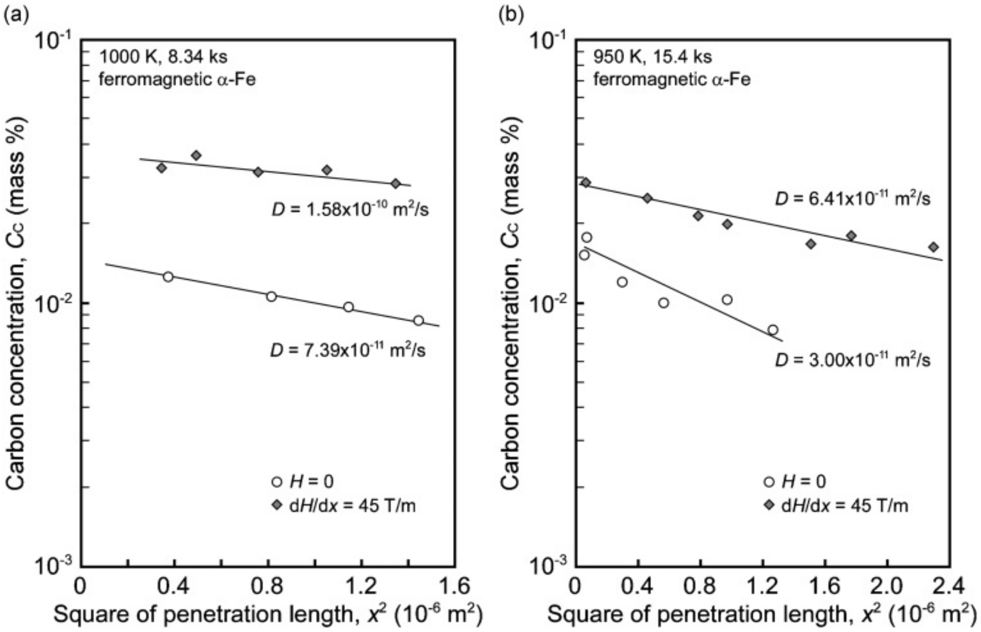

FIG. 9. The estimation of carbon diffusivities in the iron and steel diffusion couples annealed at (a) 1200 K and (b) 1000 K without and with a 45 T/m magnetic-field gradient.

volume magnetostriction constant of the ⟨100⟩ directions in γ-Fe is known to be negative as opposed to α-Fe. In other words, when a uniform magnetic field is applied, the fcc iron lattice compresses in the ⟨100⟩ direction. This would make the retardation effect of carbon diffusivity in γ-Fe by a uniform magnetic field.

B. Origin of a magnetic-field effect on carbon diffusion

The activation entropy for diffusion was found to be important for the occurring magnetic-field effect on diffusivity of carbon in iron. On the basis of the dual-occupancy model for diffusion of carbon in iron, proposed by McLellan *et al.*,[44] we will discuss the effect of a magnetic field on diffusion of carbon in iron. According to this model, the interstitial solute atoms are assumed to occupy both octahedral (O) and tetrahedral (Te) sites in bcc α-Fe, and only octahedral sites in fcc γ-Fe. The fraction of solute atoms located at octahedral sites is discussed on the basis of thermodynamics. The solutions involved in this study are very dilute, so the solute-solute interactions can be ignored and all configurations are assumed to have the same energy. Differentiating the Helmholtz free-energy F with respect to the number of occupied tetrahedral sites N_v^{Te} yields

$$\frac{dF}{dN_v^{Te}} = kT \ln \frac{N_v^{Te}}{N_v^{O}} \frac{N_v \beta_O - N_v^{O}}{N_v \beta_{Te} - N_v^{Te}} - T\Delta S + \Delta E, \quad (6)$$

where N_v^O is the number of occupied octahedral sites, N_v is the number of solvent atoms, β_O is the number of octahedral sites per solvent atoms, β_{Te} is the number of tetrahedral sites per solvent atoms, ΔS is the difference between the changes in vibrational entropies occurring when a solute atom is inserted in an octahedral site and in a tetrahedral site, $\Delta S = \bar{S}_u^{Te} - \bar{S}_u^{O}$, and ΔE is the difference between the energies per solute atom located at octahedral sites and tetrahedral sites, $\Delta E = \bar{E}_u^{Te} - \bar{E}_u^{O}$. In the equilibrium distribution, $dF/dN_v^{Te} = 0$; the equilibrium distribution can be described as

$$\frac{N_{Te}}{N_O} = \frac{\beta_O}{\beta_{Te}} \exp\left(-\frac{\Delta E}{kT}\right) \exp\left(\frac{\Delta S}{k}\right), \quad (7)$$

with the dilute-solution approximations $N_v \beta_O \gg N_v^O$ and $N_v \beta_{Te} \gg N_v^{Te}$. For the bcc lattice, $\beta_O = 3$ and $\beta_{Te} = 6$.[44] The fraction of solute atoms located at octahedral sites can be expressed by

$$\varphi_O = \frac{N_O}{N_O + N_{Te}} = 1 - \left[2 \exp\left(\frac{\Delta E}{kT}\right) \exp\left(-\frac{\Delta S}{k}\right) + 1\right]^{-1}, \quad (8)$$

and was calculated as a function of temperature. The calculated values are exhibited in Table III.[44] From the experimental result shown in Fig. 7, the diffusion entropy for carbon atoms should be decreased with increasing magnetic-field strength. We will pay particular attention to changes in the fraction of carbon located at octahedral sites with the value of ΔS. As shown in Fig. 11, this fraction is found to increase with decreasing ΔS. Accordingly, from the definition of ΔS, $\bar{S}_u^{Te}$ should be decreased more than $\bar{S}_u^{O}$ by the application of a magnetic field. This is likely to be expected because the lattice of α-Fe expands along a ⟨100⟩ direction owing to the magnetostriction under a magnetic field.[43]

TABLE III. Physical constants used for the calculations shown in Figs. 11 and 12 (Ref. 44).

Parameter	Value
$\Delta S/k$	-4.4
ΔE	30.1 kJ/mol
$D_{0,\,O\text{-}Te\text{-}O}$	3.3×10^{-7} m^2/s
$D_{0,\,Te\text{-}Te}$	2.6×10^{-4} m^2/s
$Q_{O\text{-}Te\text{-}O}$	80.8 kJ/mol
$Q_{Te\text{-}Te}$	61.5 kJ/mol
φ_{Te}	0.86

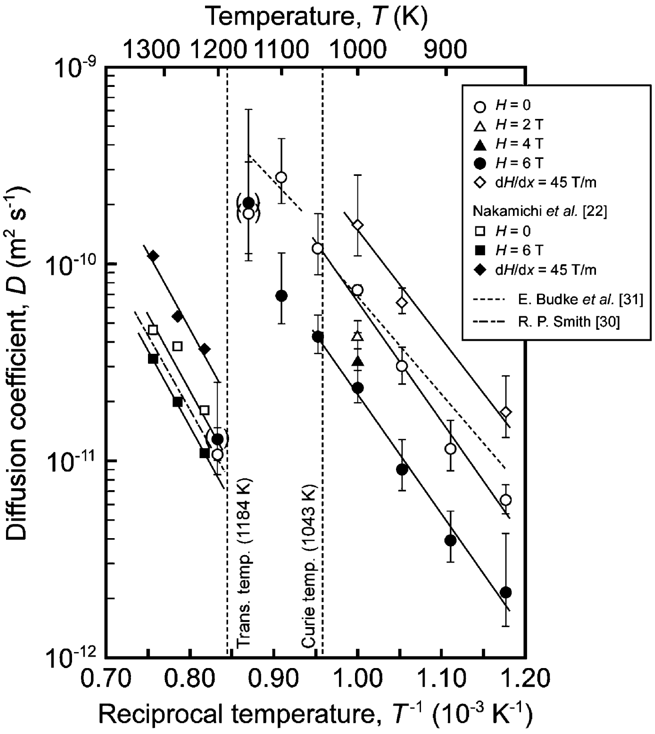

FIG. 10. Arrhenius plots of carbon diffusion coefficients in pure iron under uniform magnetic fields of 2–6 T and a magnetic-field gradient of 45 T/m. For comparison, the reported data (Refs. 22, 30, and 31), which were obtained under nonmagnetic field, are shown by the squares and the dashed lines.

In considering the diffusion of carbon in α-Fe, the carbon atoms distribute among the O and Te sites at each stage during a diffusion process. Beshers has considered the possible jumps that an interstitial atom can make in the bcc lattice.[46] The jumps are as follows: (a) The path of an atom on an O to another O will be O-Te-O; (b) an atom on a T site has two alternative paths, Te-O-Te and Te-Te.

There are three different diffusion paths of carbon in α-Fe: O-Te-O, Te-O-Te, and Te-Te routes. The direct jump between neighboring octahedral sites must involve passage through a tetrahedral site. In a solution where both O and Te sites are occupied, the observed diffusivity will be a weighted linear

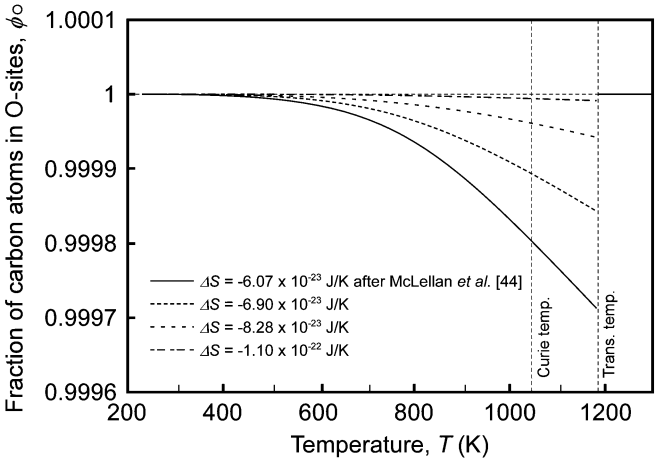

FIG. 11. The fraction of carbon atoms located in octahedral sites as a function of temperature, which was calculated with various differences between changes in vibrational entropies occurring when a solute atom is inserted in an octahedral site and in a tetrahedral site.

sum of the diffusivities of the three diffusion paths. Then the total carbon diffusivity is given by

$$D = \varphi_O D^{O\text{-}Te\text{-}O} + (1-\varphi_O) \times [\varphi_{Te} D^{Te\text{-}Te} + (1-\varphi_{Te})\, D^{Te\text{-}O\text{-}Te}], \tag{9}$$

where φ_{Te} is the fraction of atoms on *Te* sites that diffuse by the *Te-Te* mechanism. This equation can be simplified as Eq. (10), by noting that $D^{O\text{-}Te\text{-}O}$ is equal to $D^{Te\text{-}O\text{-}Te}$:

$$D = \varphi_O D^{O\text{-}Te\text{-}O} + (1-\varphi_O) \times [\varphi_{Te} D^{Te\text{-}Te} + (1-\varphi_{Te})\, D^{O\text{-}Te\text{-}O}] \tag{10}$$

The values of preexponential factors and activation energies at each diffusion path are shown in Table III. Although the fraction of carbon atoms at the tetrahedral sites is extremely small in the α-Fe temperature range, the overall diffusion coefficient is significantly affected by the carbon atoms in the tetrahedral sites because the diffusion coefficient of carbon with the *Te-Te* route is ~1000 × larger than that with the *O-Te-O* route. The overall carbon diffusion coefficients were calculated as a function of temperature with different fractions of carbon atoms located at octahedral site φ_O, and compared with the experimental results in the figure of Arrhenius plot shown in Fig. 12. For comparison, the reported data,[47] which was obtained without a magnetic field, is shown in the figure as squares. The solid line shows the calculated results for carbon diffusion using a dual-occupancy model. This is in good agreement with the experimental results of carbon diffusion coefficients without a magnetic field. Furthermore, the diffusion coefficients of carbon were calculated on the assumption that all carbon atoms are located at the *O* sites: $\varphi_O = 1$ and $\varphi_{Te} = 0$. The result calculated is shown by a dashed line in Fig. 12. This is in good agreement with the experimental results of carbon diffusion coefficients under a 6-T magnetic field. Moreover, as the fraction of octahedral site occupancies could not increase any further, the retardation effect of a magnetic field on diffusivity may be saturated at approximately a field strength of 6 T. As stated above, it is concluded that the carbon diffusivity in α-Fe is decreased with increasing *O* site occupancy owing to the application of a uniform magnetic field.

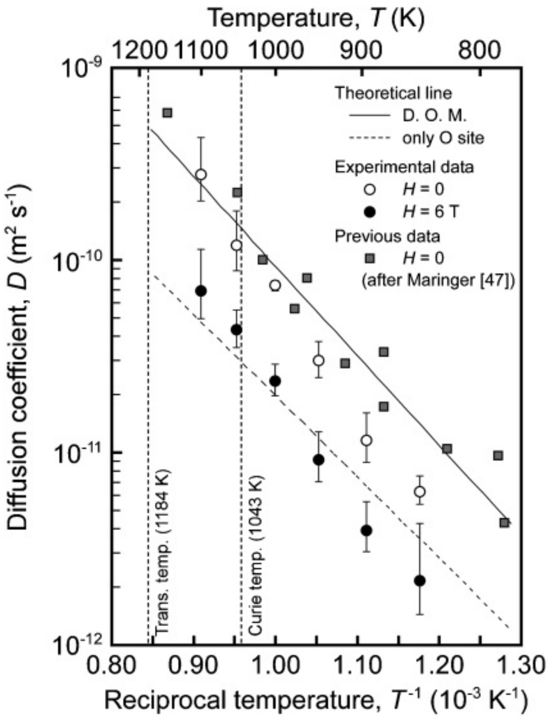

FIG. 12. The comparison between the experimentally obtained carbon diffusivities in iron and the calculated ones by the dual-occupancy model.

C. Effect of a magnetic-field gradient on diffusivity of carbon in iron

The increase in diffusivity of carbon in ferromagnetic α-Fe under a negative magnetic-field gradient can be explained from the point of view of a potential gradient owing to magnetic free-energy. The magnetic free-energy per unit volume for ferromagnetic materials is given by

$$U_M^f = -\mu_0 \left(H - \frac{N M_s}{2} \right) M_s, \tag{11}$$

where μ_0 is the magnetic permeability of vacuum, N is the demagnetizing factor, and M_s is the saturation magnetization of iron. As we can see, the negative magnetic-field gradient involves a positivemagnetic free-energy gradient in α-Fe because of a positive value of permeability for α-Fe at the annealing temperature. It is reasonable to consider that the magnetic free-energy gradient in α-Fe may produce a flux of carbon atoms toward a lower magnetic free-energy regime. Under a potential gradient, which can drive the diffusion of atoms, Fick's first law is given by

$$J = -D \left(\frac{dC}{dx} + \frac{CV}{kT}\frac{dU}{dx} \right), \tag{12}$$

where J is the flux of atoms, k is Boltzmann constant, and dU/dx is a potential gradient. From Eq. (11), the diffusion flux can be expressed by

$$J = -D\left(\frac{dC}{dx} - \mu_0 M_s \frac{CV}{kT}\frac{dH}{dx}\right). \tag{13}$$

Here, the demagnetizing factor N was ignored. Therefore, when a negative magnetic-field gradient, $(dH/dx)<0$, is applied, the total flux of carbon atoms will be increased. Conversely, the flux will be decreased in a positive magnetic-field gradient, as Nakamichi *et al.* observed.[22] This is a probable explanation for the enhancement of carbon diffusion in iron by the application of the negative magnetic-field gradient. It should be noted that, unlike under a uniform magnetic field, changes in diffusion coefficients of carbon in iron under a magnetic-field gradient are probably apparent, because a change in the driving force for diffusion owing to a magnetic-field gradient may have been measured as a variation of the diffusion coefficient in appearance.

V. CONCLUSIONS

The effects of a uniform magnetic field and a magnetic-field gradient on the carbon diffusivity in iron were experimentally investigated using a diffusion couple between pure iron and eutectoid steel (Fe-0.87 mass% C). The chief results obtained are as follows.

(a) The application of a uniform magnetic field caused a decrease in the diffusivity of carbon in α-Fe. The carbon diffusivity in ferromagnetic α-Fe was decreased by 67% under a 6-T magnetic field. This magnetic-field effect on carbon diffusion was more pronounced in α-Fe than in γ-Fe. The activation energies for carbon diffusion under nonmagnetic and magnetic fields in α-Fe were 117 ± 12 and 112 ± 12 kJ/mol, respectively. The activation energy for carbon diffusion was less dependent on a magnetic field. The magnetic field predominantly affected the frequency factor of diffusion.

(b) The logarithm of carbon diffusion coefficients in ferromagnetic α-Fe was a linear function of a magnetic-field strength. This suggests that the activation entropy of diffusion would decrease with increasing magnetic field.

(c) The decrease in carbon diffusivity, which is predominantly owing to a decrease in activation entropy for diffusion, would result from an increase in the fraction of carbon atoms located at the octahedral sites in α-Fe by the application of a uniform magnetic field.

(d) A negative magnetic-field gradient enhanced the carbon diffusion in α-Fe. This enhancement was ~115% in the magnetic-field gradient of 45 T/m $[H(dH/dx) = 2.08 \times 10^2\ \mathrm{T^2/m}]$. The activation energy for carbon diffusion in α-Fe in the magnetic-field gradient was estimated to be 100 ± 13 kJ/mol. No significant effect of a magnetic-field gradient on the activation energy was observed.

(e) The magnetic free-energy gradient in α-Fe is likely to act as a driving force for diffusion of carbon. The negative magnetic field can give rise to an increase in the flux of carbon atoms.

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