Diffusion in High-Purity Iron: Influence of Magnetic Transformation on Diffusion

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Influence of magnetic transformation on volume diffusion, dislocation diffusion, and grain boundary diffusion in high-purity iron (Fe) has been studied. The intensity of the influence on volume diffusion is found to be proportional to the change of magnetization of the Fe matrix around the first and second shells of the diffusing atom. The influence of magnetic transformation on the grain boundary diffusion and dislocation diffusion in Fe is found to be much larger than that on the volume diffusion.

1. Introduction

The oldest measurement of tracer self-diffusion in α-iron (Fe) is that by Birchenall and Mehl in 1948, which is listed in a compilation by Askill.[1] During the 1950s, the influence of magnetic transformation on self-diffusion in Fe was recognized. Many experimental and theoretical works on this topic were carried out in the 1960s. However, the traditional mechanical sectioning techniques, which limit the measurable minimum diffusion coefficient to 10^{-16} m^2/s, have mainly been used. Therefore, the self-diffusion coefficient of Fe could be determined down to only 70 K below the Curie temperature ($T_c = 1043$ K); thus, the diffusion behavior of ferromagnetic Fe was not definite.[2] However, in 1977 Hettich et al.[3] succeeded in measuring the diffusivity down to 259 K below T_c by a new technique, ion-beam sputter-microsectioning. Their work supplied a powerful tool for the study of the influence of magnetic transformation on diffusion in αFe.[4]

Below the T_c, an Arrhenius plot of diffusion coefficients in the ferromagnetic state of Fe deviates downward from the Arrhenius relationship extrapolated from the paramagnetic state. Equations describing such temperature dependence for the diffusion coefficients in the whole temperature range across the T_c have been proposed by several authors such as Ruch et al.,[5] Hettich et al.,[3] Kučera,[6] and Braun and Feller-Kniepmeier.[7] According to Ruch et al.,[5] the temperature dependence of the diffusion coefficient D can be expressed by an equation:

$$D = D_0^p \exp[-Q^p(1 + \alpha s^2)/RT] \qquad \text{(Eq 1)}$$

Here, D_0^p and Q^p are the preexponential factor and the activation energy, respectively, in the paramagnetic state.

The value of s, the ratio of the spontaneous magnetization at temperature T K to that at 0 K, has been experimentally determined by Potter[8] and Crangle and Goodman.[9] The constant α, expressing the extent of the influence of the magnetic transformation on diffusion, is given by:

$$\alpha = (\alpha_f + \alpha_m)/Q^p \qquad \text{(Eq 2)}$$

where α_f and α_m are the increments of the formation energy and the migration energy, respectively, of a vacancy due to the transformation from the paramagnetic state to the ferromagnetic state. α_f is related to the exchange integral J between a jumping atom and a nearest-neighbor atom in the equilibrium position. Let z be the coordination number, then $\alpha_f = zJ/2$ and was estimated to be 4.3 kJ/mol for Fe by Ruch et al.[5] α_m is related to the exchange integral J^* between a jumping atom in the saddle point and a nearest-neighbor atom by $\alpha_m = cJ^*$, where c is a constant. The theoretical calculation of α_m is not feasible at present due to difficulty in the estimation of J^*.

However, the value of α can be evaluated from the experimental data in the following way. Equation 1 can be rewritten as:

$$T \ln[D(T)/D_0^p] = -Q^p/R - (\alpha Q^p/R)s^2 \qquad \text{(Eq 3)}$$

Substituting the values of $D(T)$ and D_0^p from the diffusion experiments and the empirical value of $s(T)$ for pure Fe given by Potter[8] and Crangle and Goodman[9] into Eq 3, we have a plot of $T \ln[D(T)/D_0^p]$ as a function of s^2. From the slope and intercept of the linear line, α and Q^p can be obtained. In this way, Q^p is recalculated and is usually in good agreement with that determined directly.

The authors have carried out experiments on the volume diffusion of transition elements such as ^{51}Cr, ^{57}Co, ^{59}Fe, ^{95}Nb, ^{99}Mo, and ^{181}W in high-purity αFe by use of a sputter-microsectioning technique. The temperature dependence of the diffusion coefficients across the T_c was analyzed successfully by the model of Ruch et al.[5] The diffusion behavior of chromium (Cr) and cobalt (Co) in the ferromagnetic Fe is interesting due to their negative and positive magnetic moment, respectively, in Fe.[10] Furthermore, the diffusion coefficients of niobium (Nb), molybdenum (Mo),

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and tungsten (W) in Fe are useful for obtaining the basic data on ferritic heat-resisting alloys, because the addition of these elements for remarkably increasing the creep strength of steels is well known.[11] On the other hand, many experimental studies on grain boundary self-diffusion in Fe have been conducted.[12] However, a large scatter in the Arrhenius plots of the grain boundary self-diffusivities has been observed. One of the possible reasons for this is the high content of impurities like carbon, sulfur, nitrogen, oxygen, phosphorous, and boron, because these elements are known to suppress diffusion along grain boundaries.[12] The influence of the magnetic transformation on grain boundary diffusion in Fe was ambiguous, because old experiments were limited to relatively higher temperatures. Now, in this article, recent experiments on the grain boundary diffusion of ^{51}Cr, ^{57}Co, and ^{59}Fe in high-purity Fe are presented. The penetration profiles were analyzed by the type C kinetics for diffusion at lower temperatures as well as by the type B kinetics for diffusion at higher temperatures. The influence of the magnetic transformation on grain boundary diffusion was found to be much larger than that on volume diffusion. The model of Ruch et al.[5] was successfully extended to the analysis of the temperature dependence of the grain boundary diffusion coefficients across the T_c. Finally, self-diffusion along dislocations in high-purity Fe is also presented.

Fig. 1 Ahhenius plots of self-diffusion coefficients in αFe

2. Magnetic Influence on Volume Diffusion in Fe

After the work by Hettich et al.,[3] experiments on self-diffusion in αFe by the sputter-microsectioning technique were carried out by Iijima et al.[13] and by Lübbehusen and Mehrer.[14] An Arrhenius plot of the self-diffusion coefficients determined by these three works[3,13,14] is shown in Fig. 1 and is compared with those determined by the conventional mechanical sectioning techniques used in the 1960s. The self-diffusion coefficient in αFe determined by Iijima et al.[13] shows a linear Arrhenius relationship from the T_c to the α-γ transformation temperature (1184 K) with a preexponential factor 2.76×10^{-4} m²/s and an activation energy of 250.6 kJ/mol. In Fig. 1, it is noticeable that in the paramagnetic αFe the diffusion coefficients obtained by the conventional mechanical sectioning techniques are larger than those obtained by the sputter-microsectioning techniques. The mean penetration distance in the diffused specimen $2(Dt)^{1/2}$ in the former experiments was in the range of 30 to 100 μm, whereas in the latter experiments it was in the range of 1.5 to 4.4 μm.[13,14] This observation leads to the conclusion that in paramagnetic αFe the apparent self-diffusion coefficients obtained by the conventional mechanical sectioning techniques are usually affected by the enhancement effect due to dislocation diffusion.[13,14]

Figure 2 shows the plot of $T \ln[D(T)/D_0^p]$ versus s^2 for self-diffusion in the ferromagnetic αFe. The values of α and Q^p obtained from the slope and intercept of the straight line were 0.153 and 250.8 kJ/mol, respectively.[4] The value of Q^p is in good agreement with that obtained directly by the linear Arrhenius relationship in the paramagnetic αFe. Hence, by putting $α_f = 4.3$ kJ/mol,[5] $α = 0.153$, and $Q^p =$
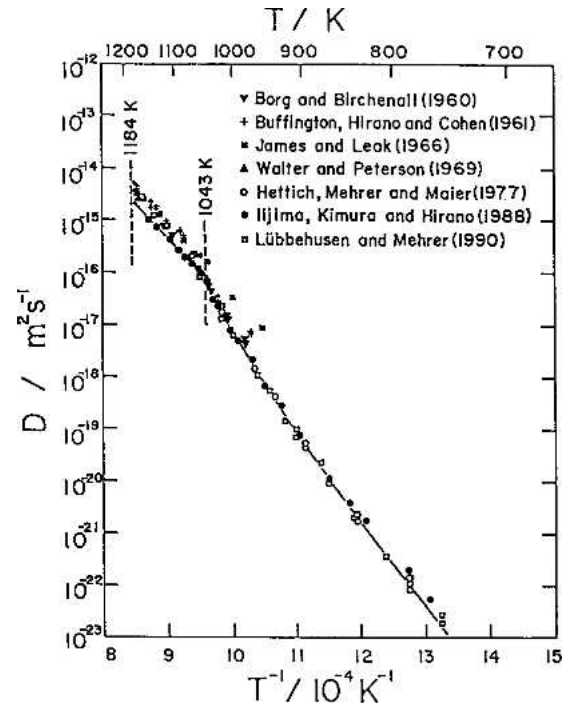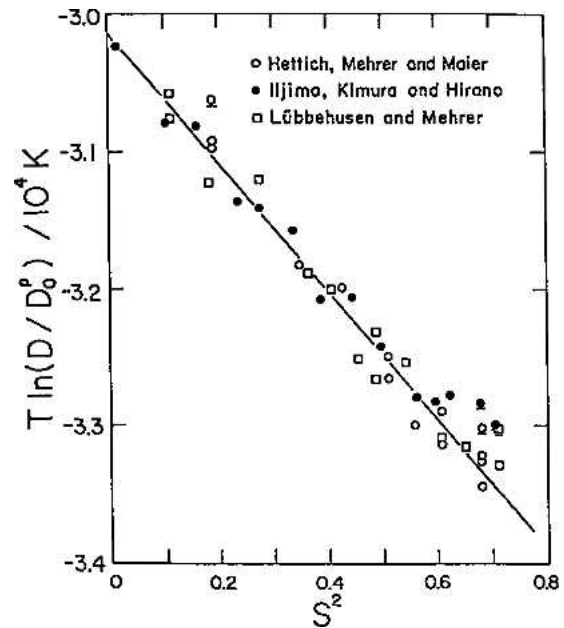

Fig. 2 Plot of $T \ln(D/D_0^p)$ versus s^2 for self-diffusion in the ferromagnetic αFe

250.6 kJ/mol into Eq 2, the increment $α_m$ for the migration energy of a vacancy is estimated to be 34.0 kJ/mol. Therefore, of the total contribution of 38.3 kJ/mol of magnetic transformation to the excess activation energy for self-diffusion in Fe, the increment of the formation energy of a vacancy was 4.3 kJ/mol (11%) and the increment of the migration energy of a vacancy was 34 kJ/mol (89%).

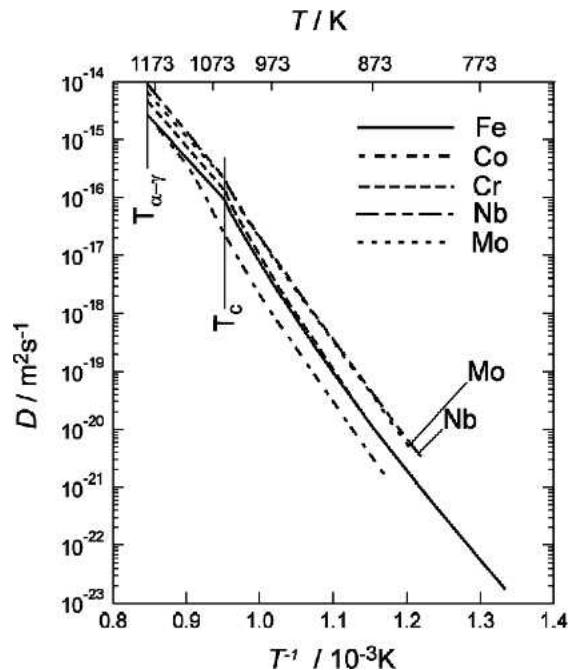The influence of magnetic transformation on the solute

Fig. 3 Temperature dependence of diffusion coefficients of ^{59}Fe, ^{51}Cr, ^{57}Co, ^{99}Mo, and ^{95}Nb in high-purity αFe

diffusion in Fe is also interesting in view of the fact that the diffusion behavior of solute atoms in the ferromagnetic αFe is connected to the change of magnetization in the Fe matrix around the solute. The temperature dependence of the diffusion coefficients of ^{59}Fe,[13] ^{51}Cr,[15] ^{57}Co,[16] ^{99}Mo,[17] and ^{95}Nb,[18] in high-purity αFe is shown in Fig. 3. The line for ^{181}W was not put in Fig. 3, because it is only slightly above the line for self-diffusion. Except for Co, the Arrhenius plots from the T_c to the α-γ transformation temperature $T_{\alpha\text{-}\gamma}$ are linear without any influence of the short-range magnetic spin ordering, whereas the Arrhenius plot for the diffusion of Co in αFe in the same temperature region approaches the linear Arrhenius line for the self-diffusion with an increase of temperature in an asymptotic manner. This means that a local magnetic field around a solute Co atom is stronger than the magnetic field of the Fe matrix and remains so even above the T_c. On the other hand, around a solute atom such as Cr, Mo, Nb, or W, the local magnetic field is weaker than that of the Fe matrix and nearly diminishes at the T_c. These experimental results support the model by Ruch et al.,[5] in which the short-range magnetic spin ordering was not taken into consideration, although its effect has been emphasized in the other models.[3,6,7]

The values of the preexponental factor D_0^p and the activation energy Q^p for these elements are summarized in Table 1. The value of α for the solute diffusion has been obtained by plotting $T \ln[D(T)/D_0^p]$ versus s^2 in the same way as self-diffusion, as shown in Fig. 2. The temperature dependence of αs^2 for self-diffusion[13] and other solutes[15-18] is shown in Fig. 4. For the self-diffusion and diffusion of Cr, Mo, Nb, and W in αFe, αs^2 decreases gradually with an increase of temperature and becomes 0 at and above the T_c of pure Fe. However, for the diffusion of Co in αFe, αs^2 is larger than that for the self-diffusion in the whole tempera-
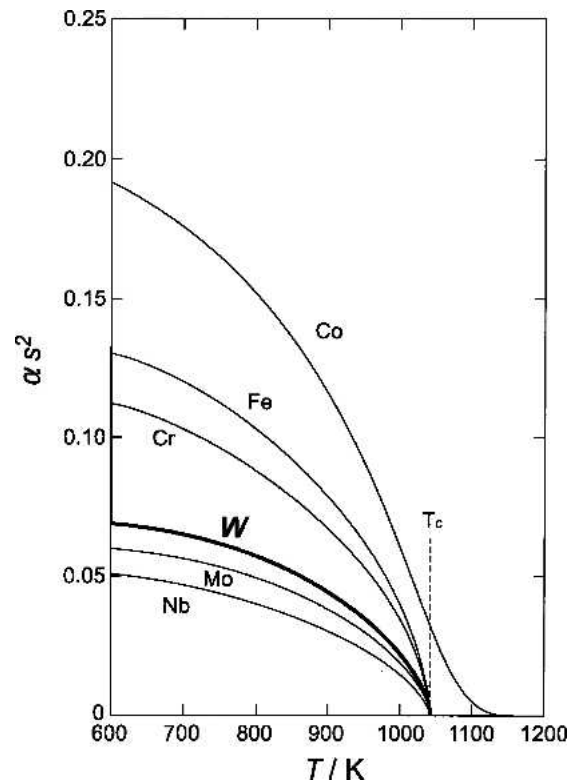

Fig. 4 Temperature dependence of αs^2 for the diffusion of transition elements in αFe

ture range and becomes 0 at and above 1140 K, which is 97 K higher than the T_c of pure Fe.

The magnitude of α is most likely related to the magnetic field around the diffusing atom. The change in magnetization ΔM is made up of a contribution arising from the influence of the impurity atom on the magnetic moment of the surrounding Fe atoms and from the contribution of the local impurity moment. Thus, ΔM is the sum of contributions from all neighbors extending out to several shells. In body-centered cubic metals, a diffusing atom jumps to a nearest-neighbor site through two barriers. The first barrier consists of the nearest neighbors. The second barrier consists of the second-nearest neighbors. According to Dever,[19] the magnetic influence on diffusion is mainly due to the increase in jumping energy through the second barrier. Drittler et al.[20] have calculated the values ΔM_n, the changes of the local moment of an Fe atom in the nth shell around a solute atom from the first to fifth shells. Figure 5 shows the plot of α against $\Delta M_{1\text{-}2}$, the sum of the magnetization changes of the first and second shells.[21] A linear relation is observed, suggesting that the activation energy for diffusion in the ferromagnetic Fe is characterized by the change in magnetization of the first-nearest and second-nearest neighbors of the diffusing atom in Fe.

3. Magnetic Influence on Grain Boundary Diffusion

As described previously, a large scatter in the Arrhenius plots of grain boundary self-diffusivities in αFe is ob-
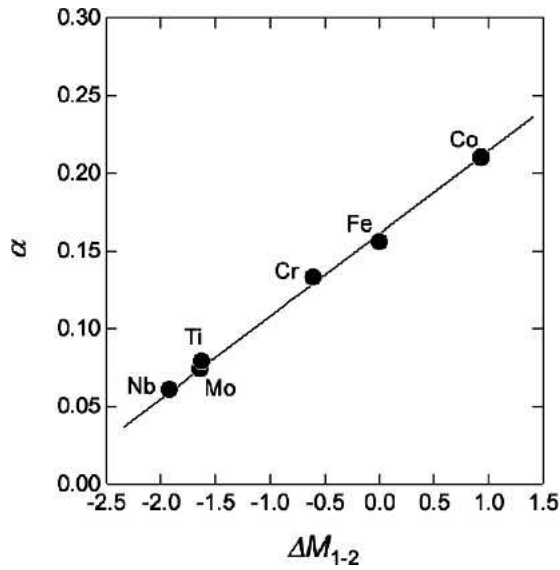
Fig. 5 Plot of α versus ΔM_{1-2}

Table 1 Preexponential factor, activation energy, and constant α for diffusion of transition elements in α-iron

Diffusant	$D_0{}^p/m^2s^{-1}$	$Q^p/kJmol^{-1}$	α
Co	2.76×10^{-4}	251	0.23
Fe	2.76×10^{-4}	250.6	0.156
Cr	3.73×10^{-4}	267.1	0.133
W	1.5×10^{-2}	287	0.086
Mo	1.48×10^{-2}	282.6	0.074
Nb	1.4×10^{-1}	299.7	0.061

served.[12] The authors prepared very high-purity Fe specimens with an average grain size of 2.5 mm. Chemical analysis showed that the impurities were: C, 0.7 mass ppm; S, 1.0 mass ppm; N, 0.7 mass ppm; O, 2.0 mass ppm; and P, 1.0 mass ppm. The grain boundary self-diffusion coefficient D_{gb} in high-purity Fe was measured in the temperature range between 523 and 703 K using type-C kinetics. Furthermore, grain boundary self-diffusivity, δD_{gb}, was measured between 873 and 1173 K using type-B kinetics. Because the Arrhenius plot of δD_{gb} showed a linear relationship above the T_c and an apparent bending across the T_c, the model of Ruch et al.[5] was applied to analyze the influence of magnetic transformation on grain boundary diffusion. From the linear Arrhenius plot of δD_{gb} above the T_c, the preexponential factor and the activation energy for grain boundary self-diffusion in the paramagnetic αFe were obtained. Then, the value of α was estimated from the plot of $T \ln[\delta D_{gb}(T)/ \delta D_{gb0}]$ versus s^2. Inserting the width of the grain boundary $\delta = 0.5$ nm into the grain boundary self-diffusion coefficient D_{gb} obtained by type-C kinetics, the temperature dependence of δD_{gb} links smoothly with that obtained by type-B kinetics over the whole temperature range, as shown in Fig. 6.
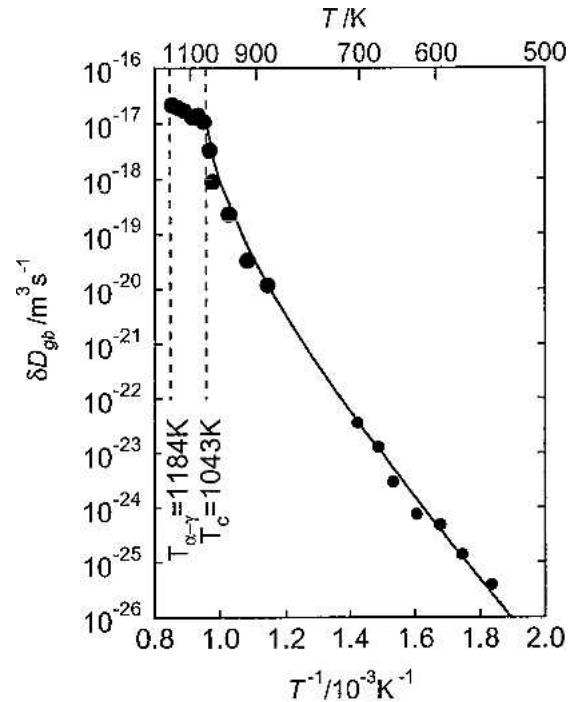

Fig. 6 Temperature dependence of δD_{gb} determined by type B and C kinetics in αFe

The temperature dependence of δD_{gb} across the T_c can be expressed by:

$$\delta D_{gb} = 6.35 \times 10^{-15} \exp[-55.7 \text{ kJ/mol}^{-1} \\ (1 + 1.28 \ s^2)/RT]m^3/s^{-1} \qquad \text{(Eq 4)}$$

The activation energy for the grain boundary self-diffusion in paramagnetic αFe, 55.7 kJ/mol, is only 0.22 of the activation energy for the volume diffusion. According to a theoretical calculation for the Σ5[001] symmetric tilt boundary,[22] the formation energy and the migration energy of a vacancy are estimated to be 97 and 49 kJ/mol, respectively. Then, the activation energy for self-diffusion through the Σ5[001] symmetric tilt boundary results in 146 kJ/mol, which is much higher than the present experimental value of 55.7 kJ/mol, suggesting that the self-diffusion through random grain boundaries in the paramagnetic αFe is very fast with a much lower activation energy than that for diffusion through symmetric tilt boundaries. Figure 7 shows an Arrhenius plots of δD_{gb} obtained by our group in comparison with those of previous authors. The grain boundary self-diffusivity in Fe obtained by our group is much higher than those of previous authors. This suggests that the previous authors have measured the diffusion through relatively slow grain boundaries.

Furthermore, the value of $\alpha = 1.28$ in Eq 4 is about eight times that of volume diffusion, showing that the influence of the magnetic transformation on the grain boundary diffusion is much larger than that on the volume diffusion. This is consistent with the theoretical calculations that the local magnetic moments of Fe atoms near the grain boundary
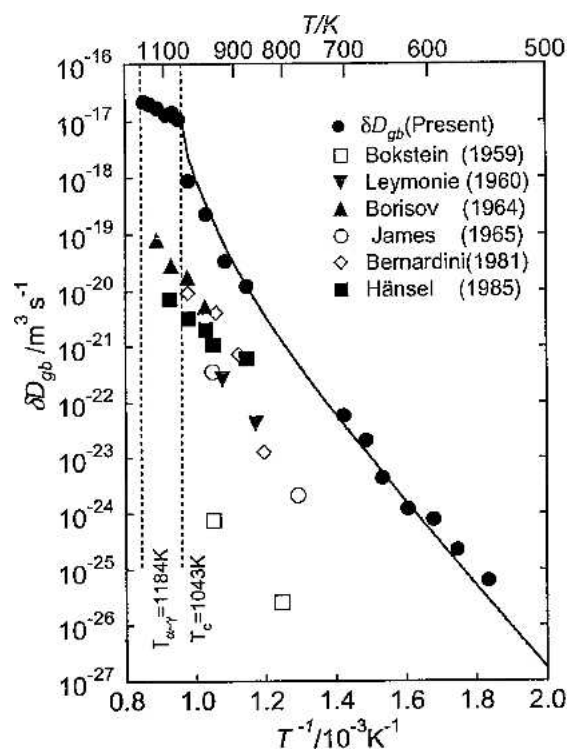
Fig. 7 Arrhenius plots of δD_{gb} obtained in this paper in comparison with those by previous authors

Fig. 8 Arrhenius plots of D_{d} obtained in this paper in comparison with that by Mehrer and Lübbehusen[27]

increase remarkably.[23,24] The experiments in the grain boundary diffusion of Cr and Co in αFe showed similar behavior to that of Fe.

4. Magnetic Influence on Dislocation Diffusion

It has been recognized that atomic migration along dislocations in metals is more rapid than through the crystal lattice itself.[25] However, experiments on dislocation diffusion in Fe as well as in other metals are uncommon. One of reasons is that the preparation of high-purity specimens with impurity-free dislocations is not easy. Using ultra-high-purity Fe made by floating zone refining under reduced pressure with dynamic hydrogen flow, an experiment in self-diffusion along impurity-free dislocations in Fe has been carried out.[26] The penetration profiles were analyzed by the type-C kinetics for diffusion at temperatures below 753 K as well as by the type-B kinetics for diffusion at temperatures above 853 K, as was also done in the case of grain boundary diffusion. For type-B kinetics, the effective radius a of the dislocation pipe is assumed to be 0.5 nm, which is a value that is often used.[25]

Figure 8 shows Arrhenius plots of self-diffusion coefficients D_{d} along dislocations in αFe. Experimental results by Mehrer and Lübbehusen[27] are also shown in Fig. 8. Above 900 K, the self-diffusion coefficient along dislocations increases remarkably with increasing temperature. This increase near the T_{c} is anomalously large in comparison with
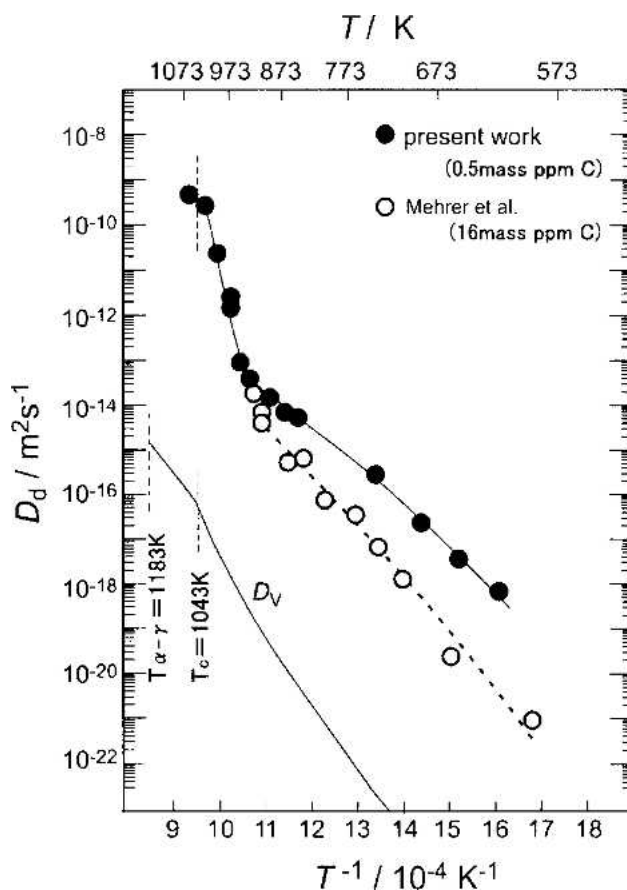
the increase in the volume diffusion coefficient D_{v} seen in Fig. 8. It seems that the very large increase of the diffusion coefficient is caused by the disappearance of the magnetic moment of Fe atoms located at the dislocation core near the T_{c}. The magnetic moment is sensitive to the atomic distance. Then, the influence of a magnetic transformation on diffusion along dislocations and grain boundaries is larger than that on diffusion through the crystal lattice. Furthermore, it is noticed that the magnitude of aD_{d} and its temperature dependence are quite consistent with those of δD_{gb} obtained by previous authors and shown in Fig. 7. This supports the view that the grain boundary self-diffusivities measured by previous authors are due to the diffusion through relatively slow grain boundaries.

5. Summary

The temperature dependence of the volume diffusion coefficient and the grain boundary diffusivity in αFe across the T_{c} is expressed successfully by the model of Ruch et al.[5] The magnetic influence on the grain boundary diffusion and dislocation diffusion in Fe is much larger than that on the volume diffusion.

Acknowledgments

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