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Determination of diffusion coefficient of oxygen in α-iron from internal oxidation measurements in Fe–Si alloys

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The diffusion coefficient of oxygen in α-iron was determined by internal oxidation measurements on iron alloys with various contents of silicon in a temperature range from 1073 to 1173 K with particular attention to the effect of oxide particles in the oxidation layer. The oxide in the oxidation layer and the concentration of silicon present as an oxide, as well as the rate constant for penetration of the oxidation front were determined. The diffusion coefficient of oxygen in the layer, D_O^{IO}, calculated using the rate equation for internal oxidation, increases with the increase in volume fraction of the oxide, f^{IO}. This result indicates that the existence of oxide particles accelerates oxygen diffusion. Therefore, the diffusion coefficient of oxygen in α-iron is determined by extrapolating D_O^{IO} to $f^{IO} = 0$, giving good agreement with results obtained in our recent investigations.

1. Introduction

When iron alloys are used at elevated tempertures, its oxidation cannot be avoided even under conditions of low oxygen chemical potential. The diffusion coefficient of oxygen is important in determining oxidation behaviour of iron alloys. However, usual methods, such as a diffusion couple and the thin layer method, cannot be applied to its determination mainly because the affinity of iron for oxygen is high and the solubility of oxygen is very low compared with the solubility of carbon or nitrogen in iron and its alloys.

From internal oxidation measurements, Swisher and Turkdogan [1] have shown that the diffusion coefficient of oxygen in iron alloys can be calculated using the concentration of dissolved oxygen. So far, very little attention has been paid to the influence of oxide particles on the diffusion coefficient of oxygen. The present authors [2, 3] have pointed out that such a diffusion coefficient varies with the volume fraction of the oxide and determined the diffusion coefficient of oxygen in γ-iron. However, there are few investigations of the diffusion coefficient in α-iron [4, 5].

The purpose of the present study is to determine the diffusion coefficient of oxygen in α-iron from internal oxidation measurements in Fe–Si alloys. Special attention has been given to the effect of oxide particles formed in the internal oxidation layer on the diffusion coefficient of oxygen. Furthermore, the measured diffusion coefficient of oxygen is discussed by comparing with those obtained in our previous investigations of Fe–Al [4] and Fe–Ti [5] alloys.

2. Materials and experimental procedure

Four iron alloys containing between 0.07 and 0.40 wt % silicon were prepared by vacuum melting. Their chemical compositions are listed in Table I. Specimens of approximately 5 mm × 5 mm × 4 mm with an average grain diameter of 85 μm were internally oxidized in the temperature range from 1073 to 1173 K, the temperature being controlled within ±2 K during oxidation. The internal oxidation was carried out using a mixture of equal amounts of iron and Fe_2O_3 powders. The structure and the thickness of the internal oxidation layer were observed on the cross-sections of the specimens subjected to the internal oxidation with an optical microscope.

The oxide formed in the oxidation layer was extracted by a bromine–alcohol method [3, 5] and subsequently studied by X-ray diffraction to identify the oxide. The concentration profile of silicon in the oxidized specimens was observed by an electron probe microanalyser (EPMA), (Hitachi X-650 type). The experimental procedure has been reported in detail elsewhere [2–5].

3. Results

Fig. 1 shows a typical microstructure of the Fe–0.07 wt % Si alloy internally oxidized at 1123 K for 180 ksec. S, F and E indicate the specimen surface, the internal oxidation front, and the thickness of the internal oxidation layer, respectively. The oxidation front penetrates in parallel with the specimen surface. A similar microstructure has been observed in Fe–Al

TABLE I Chemical compositions of the alloys (wt %)

Alloy	Si	C	Mn	P	S
Fe–0.07 Si	0.07	0.002	0.004	0.003	0.006
Fe–0.12 Si	0.12	0.002	0.003	0.003	0.006
Fe–0.18 Si	0.18	0.010	0.003	0.001	0.004
Fe–0.40 Si	0.40	0.004	0.004	0.001	0.003

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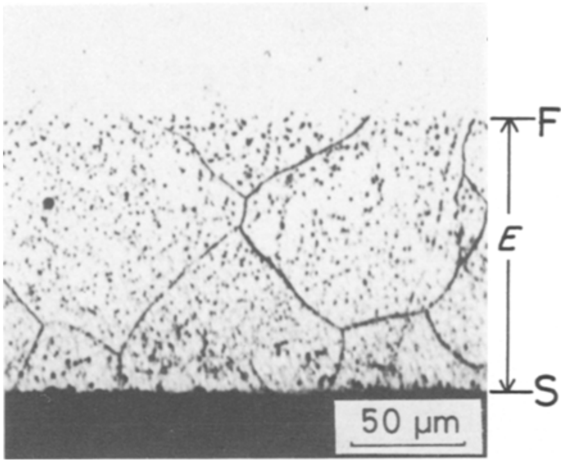

Figure 1 A typical microstructure of an Fe–0.07 wt % Si alloy internally oxidized at 1123 K for 180 ksec. S, F, and E indicate the specimen surface, the internal oxidation front, and the thickness of the internal oxidation layer, respectively.

[4] and Fe–Ti [5] alloys. E increases as either the oxidation time or the temperature increases.

The variation of the square of the thickness, E^2, of the internal oxidation layer with the oxidation time, t, is shown in Fig. 2, indicating a parabolic rate law

$$E^2 = K_p t \qquad (1)$$

where K_p is the rate constant for penetration of the oxidation front. K_p decreases with the increase in silicon content. These results suggest that the internal oxidation of the present alloys is controlled by a diffusion process.

Fig. 3 gives the temperature dependence of K_p. One can easily see that K_p is expressed as

$$K_p = K_p^* \exp\left(-\frac{Q_K}{RT}\right) \qquad (2)$$

K_p^* is a preexponential factor, Q_K the activation energy for penetration of the internal oxidation front, T the oxidation temperature, and R the gas constant. The measured values of K_p^* and Q_K are listed in Table II. The Q_K values are close to those reported for Fe–Al [4] and Fe–Ti [5] alloys in the α-phase region.

The oxide extracted from the oxidation layer was studied by X-ray diffraction. No diffraction peak was observed. Ashby and Smith [6] have shown that the oxide formed in Cu–Si alloys by internal oxidation is amorphous SiO_2. Therefore, the oxide formed in the present alloys is most probably amorphous SiO_2, giving the atom ratio of oxygen to silicon of 2.0.

TABLE II Values of the preexponential factor, K_p^*, and the activation energy, Q_K, for penetration of the internal oxidation front in Fe–Si alloys

Alloy	Preexponential factor, K_p^* ($m^2 sec^{-1}$)	Activation energy for penetration, Q_K ($kJ mol^{-1}$)
Fe–0.07 Si	4.45×10^{-5}	189 ± 9
Fe–0.12 Si	2.41×10^{-5}	187 ± 10
Fe–0.18 Si	6.08×10^{-5}	200 ± 16
Fe–0.40 Si	9.62×10^{-6}	189 ± 22

A typical concentration profile of silicon in the Fe–0.40 wt % Si alloy internally oxidized at 1123 K for 180 ksec is shown in Fig. 4. Since the fluctuation of X-ray intensity with the specimen is ascribed to oxide particles formed, the change in the X-ray intensity in the layer does not mean a change in the silicon concentration. The silicon concentration in the unoxidized region increases up to its original concentration as the distance from the oxidation front increases. This result indicates the counter-diffusion of silicon, i.e. the diffusion of silicon to the oxidation front from the bulk alloy.

4. Discussion

4.1. Internal oxidation kinetics

The kinetics of the internal oxidation have been theoretically discussed by many investigators [7–9]. On the basis of their treatments we propose a rate equation for the internal oxidation in the absence of an external oxidation layer as

$$E^2 = \frac{2N_O^S D_O^{IO}}{\nu N_B^{IO}} t \qquad (3)$$

Here, N_O^S is the oxygen concentration at the specimen surface, D_O^{IO} the diffusion coefficient of oxygen in the oxidation layer, N_B^{IO} the concentration of the alloying element, B, in the oxidation layer, and ν the atomic ratio of oxygen to B in the oxide. For alloys with

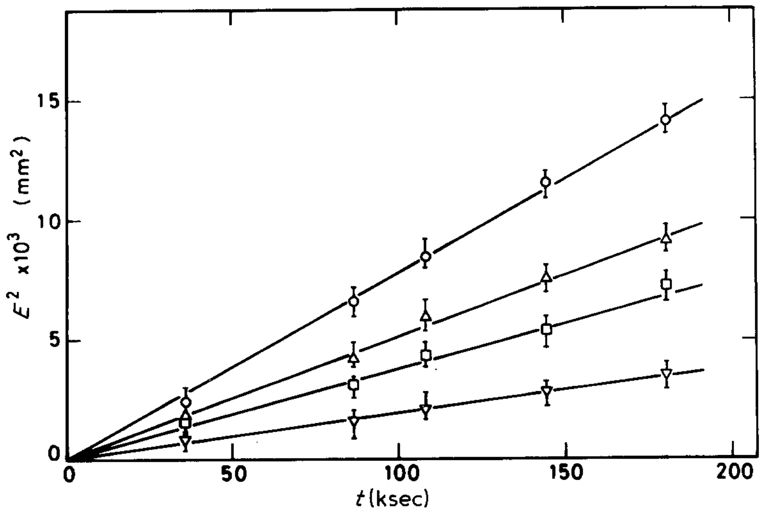

Figure 2 Square of the thickness of the internal oxidation layer as a function of the oxidation time in Fe–Si alloys internally oxidized at 1123 K. (○) Fe–0.07 Si; (△) Fe–0.12 Si; (□) Fe–0.18 Si; (▽) Fe–0.40 Si.

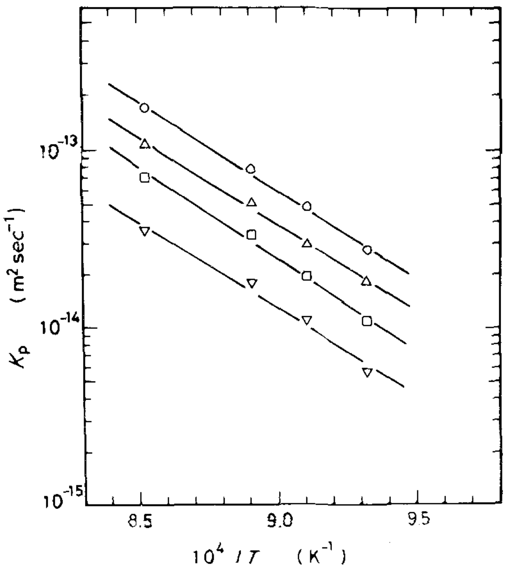

Figure 3 Temperature dependence of the rate constant for penetration of the oxidation front. (○) Fe-0.07 Si; (△) Fe-0.12 Si; (□) Fe-0.18 Si; (▽) Fe-0.40 Si.

known N_O^S, N_B^{IO} and v, D_O^{IO} can therefore be calculated from internal oxidation measurements.

When the counter-diffusion of B is negligible compared with the inward diffusion of oxygen, N_B^{IO} is equal to its original concentration, N_B^0. However, in general cases N_B^{IO} is higher than N_B^0 due to the counter-diffusion of B. In such cases z, as given by a following equation, is not much larger than unity

$$z = \frac{E}{2(D_B t)^{1/2}} \qquad (4)$$

N_B^{IO} can be described by

$$N_B^{IO} = \beta N_B^0 \qquad (5)$$

Here, β is the enrichment factor given by

$$\beta = \frac{1}{F(z)} \qquad (6)$$

where

$$F(z) = \pi^{1/2} z \exp(z^2) \operatorname{erfc}(z) \qquad (7)$$

Then one can evaluate N_B^{IO} using Equations 4–7 for alloys with known D_B. On the other hand, for alloys in which D_B is unknown N_B^{IO} should be determined experimentally, for instance, using chemical or EPMA analysis [2–5].

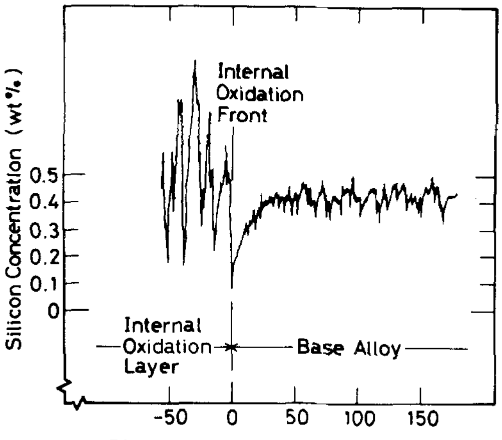

Figure 4 Concentration profile of silicon in an Fe-0.40 wt% Si alloy internally oxidized at 1123 K for 180 ksec (E = 60.8 μm).

TABLE III Values of the enrichment factor, β, and the parabolic rate constant, r

Alloy	Temperature T (K)	Enrichment factor, β	Parabolic rate constant, r ($\times 10^{-2}$)
Fe 0.07 Si	1173	1.12	3.74
	1123	1.09	2.98
	1098	1.09	2.63
	1073	1.09	2.30
Fe 0.12 Si	1173	1.17	2.79
	1123	1.14	2.23
	1098	1.13	1.96
	1073	1.13	1.72
Fe 0.18 Si	1173	1.23	2.22
	1123	1.18	1.79
	1098	1.20	1.56
	1073	1.20	1.37
Fe 0.40 Si	1173	1.36	1.47
	1123	1.31	1.14
	1098	1.30	1.01
	1073	1.33	0.87

4.2. Silicon concentration in the internal oxidation layer

In this investigation we calculated β using the data on D_{Si} [10]. The obtained values of β, listed in Table III, are slightly larger than unity. To check whether or not these values are correct, the silicon concentration in the oxidation layer was evaluated by graphically integrating the concentration profile of silicon in the unoxidized region in the vicinity of the oxidation front as shown in Fig. 4. We have shown that such a graphical integration provides nearly the same solute concentration to that determined by chemical analysis in Fe–Al alloys [3, 4]. The measured values of β are 1.09 ± 0.04, 1.14 ± 0.04, and 1.27 ± 0.05 for Fe–0.12, 0.18, and 0.40 wt% Si alloys oxidized at 1123 K, respectively. These β values are in good agreement with calculated ones shown in Table III, suggesting that the measured values are correct in the present alloys. A similar solute enrichment in the oxidation layer has been observed in some iron alloys [2–5].

4.3. Diffusion coefficient of oxygen in the oxidation layer

We have shown that in iron alloys internally oxidized using a powder mixture of Fe and Fe_2O_3 the oxygen concentration at the specimen surface, N_O^S, is controlled by a reaction in equilibrium with Fe and FeO in the α-phase region [5] as well as in the γ-phase region [3]. We evaluated N_O^S using the thermodynamic data on both the disslocation of FeO and the solution of oxygen in α-iron. The obtained values of N_O^S, given in Table IV, were used for calculation of the diffusion

TABLE IV Oxygen concentration, N_O^S, at the specimen surface

Temperature (K)	1173	1123	1098	1073
Oxygen concentration N_O^S (mol fraction, $\times 10^{-6}$)	8.86	5.51	4.28	3.28

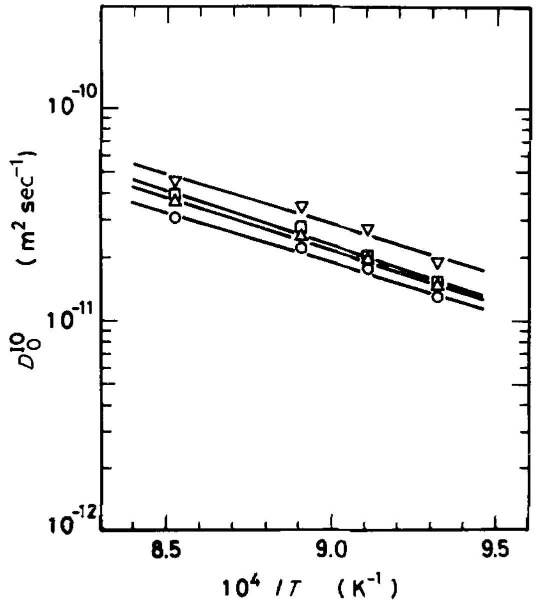

Figure 5 Temperature dependence of the diffusion coefficient of oxygen in the internal oxidation layer. (○) Fe–0.07 Si; (△) Fe–0.12 Si; (□) Fe–0.18 Si; (▽) Fe–0.40 Si.

coefficient of oxgyen, D_O^{IO}, in the oxidation layer according to Equation 3.

Fig. 5 shows the temperature dependence of D_O^{IO} for Fe–Si alloys, leading to the following equation

$$D_O^{IO} = A^{IO} \exp\left(-\frac{Q_O^{IO}}{RT}\right) \qquad (8)$$

where A^{IO} and Q_O^{IO} are the frequency factor and the activation energy for diffusion of oxygen in the internal oxidation layer, respectively. One should distinguish D_O^{IO} from the diffusion coefficient of oxygen in α-ion, because D_O^{IO} is the diffusion coefficient in the layer where the oxide particles exist. The measured values of A^{IO} and Q_O^{IO} are listed in Table V. These values are close to those reported in Fe–Al [4] and Fe–Ti [5] alloys.

Wagner [7] has defined a parabolic rate constant, r, as

$$r = \frac{E}{2(D_O^{IO}t)^{1/2}} \qquad (9)$$

TABLE V Values of the frequency factor, A^{IO}, and the activation energy, Q_O^{IO}, for diffusion of oxygen in the internal oxidation layer of Fe–Si alloys

Alloy	Frequency factor, A^{IO}, $\times 10^{-7}$ ($m^2 sec^{-1}$)	Activation energy Q_O^{IO} (kJ mol^{-1})
Fe–0.07 Si	2.36	87.6 ± 8.3
Fe–0.12 Si	2.46	86.2 ± 8.4
Fe–0.18 Si	8.97	97.9 ± 13.5
Fe–0.40 Si	4.37	89.0 ± 16.3

By combining Equations 1 and 9, we can rewrite r as

$$r = \frac{1}{2}\left(\frac{K_p}{D_O^{IO}}\right)^{1/2} \qquad (10)$$

As shown in Table III, the calculated r values are much smaller than unity, suggesting that Equation 3 is valid for the rate equation of the internal oxidation in the Fe–Si alloys.

In Fig. 6 D_O^{IO} is plotted as a function of volume fraction of the oxide, f^{IO}, in the oxidation layer, where f^{IO} was calculated from N_{Si}^{IO} using β given in Table III. D_O^{IO} increases linearly with increasing f^{IO} as expressed by

$$D_O^{IO} = D_O + bf^{IO} \qquad (11)$$

where D_O and b are constants. A similar proportionality has been found in iron [2–5] and nickel [11] alloys. These results indicate that the presence of the oxide particles apparently enhances the oxygen diffusion. The diffusion of oxygen in the oxidation layer may be controlled mainly by those in the matrix metal, the matrix–oxide interface, and the oxide. The diffusion in oxides is usually negligible compared with those in the others. As f^{IO} increases, the effective area of the matrix metal for oxygen diffusion decreases, while the area of the interface increases. The reduction in area of the matrix metal may depress the oxygen diffusion, whereas the increase in area of the interface would enhance the oxygen diffusion. In the oxidation layer where small oxide particles disperse, the latter effect is dominant, so that D_O^{IO} increases as f^{IO} increases.

4.4. Diffusion coefficient of oxygen in α-iron

D_O in Equation 11 means the diffusion coefficient of

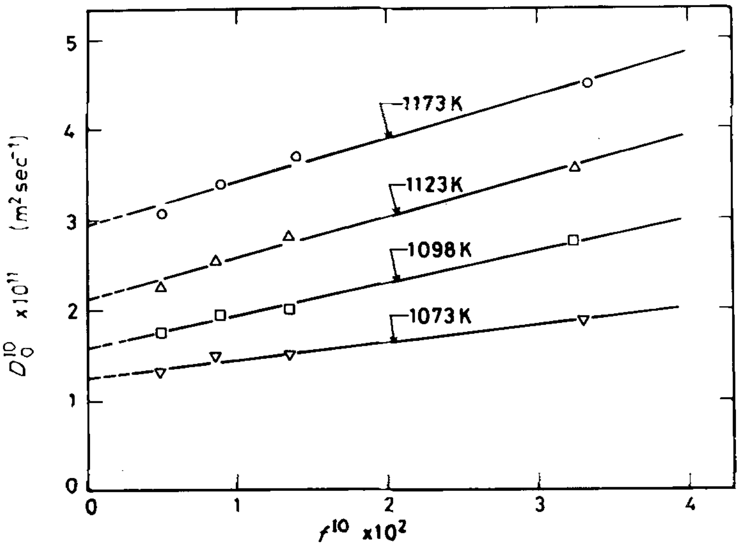

Figure 6 Diffusion coefficient of oxygen in the internal oxidation layer as a function of volume fraction of the oxide.

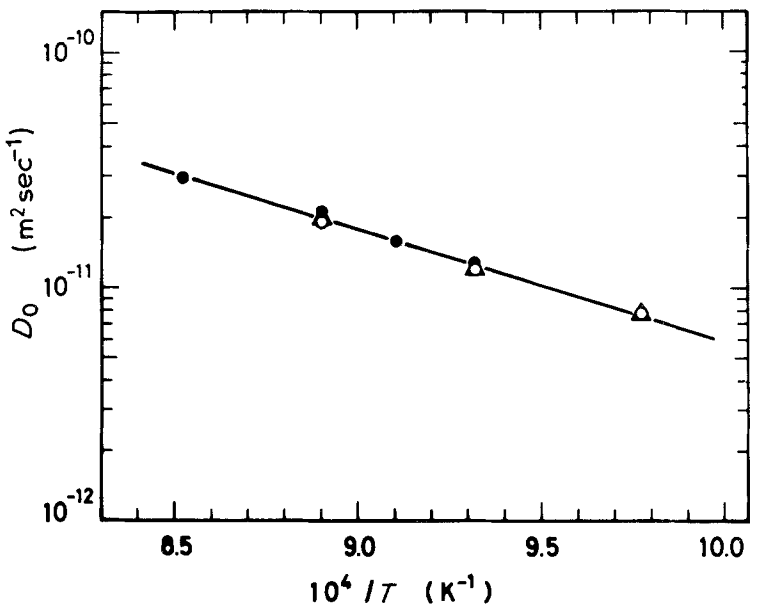

Figure 7 Temperature dependence of the diffusion coefficient of oxygen in α-iron in the present study of (●) Fe–Si alloys as well as those in our previous investigations of (△) Fe–Al [4] and (○) Fe–Ti [5] alloys.

oxygen in the matrix metal, α-iron. D_O was, therefore, determined by extrapolating D_O^{IO} to $f^{IO} = 0$ as shown in Fig. 6. The temperature dependence of D_O is shown in Fig. 7, in which the data obtained in Fe–Al [4] and Fe–Ti [5] alloys are also given. There is no significant difference in D_O for Fe–Al, Fe–Ti, and Fe–Si alloys at each temperature. This fact indicates that the internal oxidation measurement is an important method in evaluating the diffusion coefficient of oxygen in iron alloys. Thus using the data on these three alloys we determined the temperature dependence of D_O as

$$D_O = \left(2.91 \begin{matrix} +3.40 \\ -1.57 \end{matrix}\right) \times 10^{-7} \times \exp\left(-\frac{89.5 \pm 7.2\ (\mathrm{kJ\,mol^{-1}})}{RT}\right) \mathrm{m^2\,sec^{-1}} \quad (12)$$

The measured activation energy for diffusion of oxygen is close to that for the diffusion of nitrogen ($79.1\ \mathrm{kJ\,mol^{-1}}$) [12].

5. Conclusions

The internal oxidation measurements of Fe–0.07, 0.12, 0.18, and 0.40 wt% Si alloys were made in the temperature range from 1073 to 1173 K to discuss the kinetics of the internal oxidation, and to determine the diffusion coefficient of oxygen in α-iron. The internal oxidation front advances in parallel with the specimen surface. The internal oxidation process in Fe–Si alloys follows a parabolic rate law, indicating that the internal oxidation is controlled by a diffusion process of oxygen in the alloy. The counter-diffusion of silicon results in an increase in silicon concentration in the oxidation layer. The calculated silicon concentration agrees with that determined by EPMA analysis. The oxide formed in the oxidation layer is amorphous SiO_2. The diffusion coefficient of oxygen in the internal oxidation layer, D_O^{IO}, calculated from the rate equation for the internal oxidation, is proportional to the volume fraction of the oxide, f^{IO}. Furthermore, the diffusion coefficient of oxygen in α-iron, D_O, was evaluated by extrapolation of D_O^{IO} to $f^{IO} = 0$. The measured value of D_O is in good agreement with those obtained in Fe–Al and Fe–Ti alloys [4, 5]. Hence, its temperature dependence was determined using the data in these three alloys and can be expressed as in Equation 12.

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