W diffusion in paramagnetic and ferromagnetic #-Fe

R. A. Pérez & D. N. Torres

Springer

Springer

W diffusion in paramagnetic and ferromagnetic α-Fe

R.A. Pérez · D.N. Torres

Abstract Diffusion of W in the 723–1153 K temperature range both in paramagnetic and ferromagnetic α-Fe was studied, diffusion couples were manufactured by W evaporation onto high-purity Fe samples. Measurements were made using the Heavy Ion Rutherford Backscattering (HIRBS) technique as the analysis tool. A straight Arrhenius plot was obtained in the paramagnetic region with a break at the Curie temperature (1043 K) followed by a curved plot at lower temperatures as a product of the effect of ferromagnetism on diffusion. A straight Arrhenius plot was obtained in the paramagnetic region with a break at the Curie temperature (1043 K) followed by a curved plot at lower temperatures resulting from the effect of ferromagnetism on diffusion. A previous developed model for the diffusion of non-magnetic impurities in ferromagnetic Fe fits the data perfectly well, giving a temperature dependent diffusivity according to

$$D(T) = 2.3 \times 10^{-6}$$
$$\times \exp\left[-\frac{(215\ \mathrm{kJ\,mol^{-1}}) \times (1 + 0.176s^2)}{RT}\right] \mathrm{m^2\,s^{-1}}$$

R.A. Pérez (✉) · D.N. Torres
Departamento de Materiales, Comisión Nacional de Energía
Atómica (CNEA), Avenida Libertador 8250, 1429 Buenos Aires,
Argentina
e-mail: rodperez@cnea.gov.ar
Fax: +54-011-67727362

R.A. Pérez
Consejo Nacional de Investigaciones Científicas y Técnicas
(CONICET), Buenos Aires, Argentina

1 Introduction

It is well established in the literature that α-Fe self-diffusion is strongly affected by ferromagnetism [1, 2]. Self-diffusion coefficients follow an Arrhenius law in the paramagnetic region, between the phase transition temperature, $T_{\alpha/\beta} = 1184$ K, and the Curie temperature, $T_C = 1043$ K. In the ferromagnetic region, a departure from such a law is observed, consisting in a break at T_C followed by a soft upward curvature in the Arrhenius plot with smaller diffusion coefficients than the linear extrapolation of the paramagnetic ones, due to the effect of the ferromagnetic alignment.

Based on the work by Girifalco [3], which describes the effects of ordering on diffusion, Ruch et al. [4] have fitted this temperature dependence of the self-diffusion coefficient as

$$D(T) = D_0^p \exp\left[-Q^p\left(1 + \alpha s(T)^2\right)/RT\right] \qquad (1)$$

where D_0^p is the pre-exponential factor, Q^p is the activation energy, both in the paramagnetic state; $s(T)$ is the ratio of the spontaneous magnetization at temperature T to that at 0 K (reduced magnetization) which has been experimentally determined by Crangle and Goodman [5]; α is a dimensionless constant composed of two additive terms, representing the effect of magnetic ordering upon formation energy (α_f), and migration energy (α_m):

$$\alpha = \alpha_m + \alpha_f \qquad (2)$$

Let us note that at 0 K, $s(T = 0) = 1$, the spin alignment is complete and, consequently, the expression between parentheses in (1) reaches its maximum value $(1 + \alpha)$.

Table 1 Diffusion parameters for substitutional diffusers in α-Fe

	D_0^p [m^2 s^{-1}]	Q^p [kJ mol^{-1}]	α	$Q^p \cdot \alpha$ [kJ mol^{-1}]	μ_{dip} [μ_0][a]
Sn	6.0×10^{-6}	190	0.23	43 ± 4	0
Sb	1.3×10^{-5}	202	0.20	40 ± 4	0
Nb	5.0×10^{-5}	252	0.14	35 ± 5	0
W	2.3×10^{-6}	216	0.176	38 ± 5	0
As	1.0×10^{-5}	197	–	–	0
Fe	2.7×10^{-4}	251	0.156	39 ± 5	2.17 ± 0.01
Co	–	–	0.23	57.6 ± 5	1.71 ± 0.16
Cr	4×10^{-3}	267	0.14	37.5 ± 4	-3.46 ± 0.33

[a] μ_0 is the Bohr magneton

This behaviour was also observed when diffusion of magnetic impurities Co [6, 7], Cr [8] and Ni [9] where measured in a long enough temperature range. An empirical correlation between the magnetic moment of the impurity in the α-Fe matrix and the value of α used to fit the experimental data was established, so that to higher magnetic moments (listed as μ_{dip} in Table 1) correspond higher α's [7].

The present work, devoted to W, is part of a systematic study of diffusion of non-magnetic impurities in the α-Fe matrix recently initiated by us, also including As [10], Nb [11], Sb [12], Sn [13] and W (this work) in α-Fe matrix. All these non-magnetic elements play an important role as constituents and/or contaminants in low-alloyed steels, their diffusivities in α-Fe being indispensable input data in order to model and understand mechanisms such as precipitation and coarsening, temper embrittlement, etc.

At the beginning we expected an effect of ferromagnetism upon diffusion involving rather low α values, according to the proposal by Hirano et al. [7]; this, however, was not observed (see Table 1). Thus we prefer to use the quantity αQ^p rather than α given its simple physical meaning: it is the maximum increment (at 0 K) in the activation energy due to ferromagnetism $\alpha Q^p = \Delta Q_{\text{formation}} + \Delta Q_{\text{migration}}$. When such a parameter is calculated from experiment, an almost constant value $\alpha Q^p \approx 39 \pm 5$ kJ mol^{-1} is obtained.

In summary, here we measure the W diffusion in α-Fe, therefore increasing the available data of diffusion coefficients of non-magnetic impurities in this matrix, all in the context of the above introduced model.

2 Experimental procedure

Polycrystalline samples of 99.9% pure α-Fe were used; details on impurity content are reported in Table 2.

Discs of about 10 mm in diameter and 3 mm thick were mechanically polished and subjected to 3–5 annealing cycles 5 hours long at 1473 K, followed by 6 days at 1163 K in order to increase the grain size. The final grain size was

Table 2 Fe samples impurity contents in µg g^{-1}

Symbol	µg g^{-1}	Symbol	µg g^{-1}
Al	0.24	Ni	16.0
As	1.6	Nb	0.45
Bi	0.014	P	4.3
B	2.8	K	0.56
Ca	0.24	Se	⟨0.1
Cl	1.6	Si	16
Cr	5.1	Na	0.73
Co	19.0	Sr	⟨0.1
Cu	5.3	S	5.0
Ga	0.54	Sn	0.16
Pb	0.022	Ti	0.34
Li	0.004	W	0.11
Mg	0.050	V	0.08
Mn	4.4	Zn	0.75
Mo	0.65	Zr	0.018

around 500 µm. After that, the samples were re-polished with diamond paste decreasing the particle size up to a quarter of a µm, in order to obtain a specular surface. Then the samples were cleaned with acetone and ultra-sound followed by de-ionized water.

Diffusion pairs were built by evaporation of high-purity W, 99.9%, onto the α-Fe samples surface, using an ion gun system in a vacuum better than 10^{-4} Pa; 15 nm thick films were so obtained.

Diffusion anneals were performed in sealed quartz tubes filled with high-purity argon. Diffusion temperatures were controlled within ± 1 K with Pt-PtRd S type thermocouples.

Quantitative HIRBS (Heavy Ion Rutherford Backscattering Spectrometry) analysis was performed with ^{9}F, 38 MeV ion beam in the tandem Van der Graaf facility of the Physics Department of the Argentine Atomic Energy Commission.
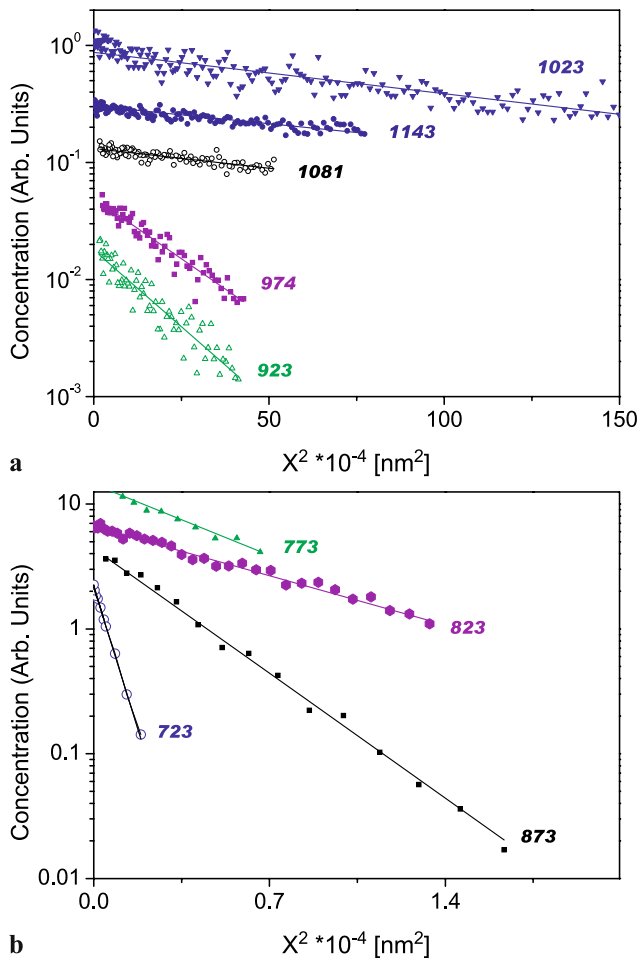
Fig. 1 Diffusion profiles for measurements listed in Table 3

Table 3 Measured diffusion coefficients for W in ferromagnetic α-Fe

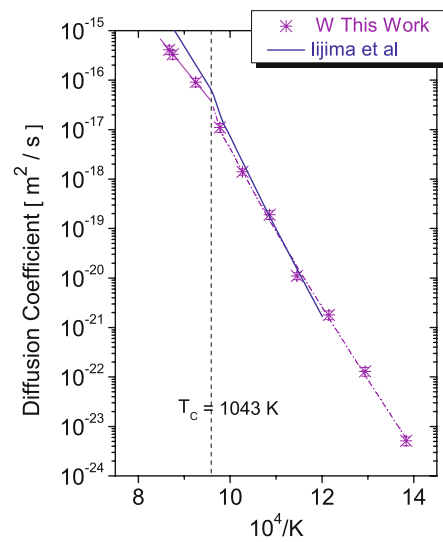| Temperature (K)	Annealing time (10^4 s)	D ($m^2 s^{-1}$)
723	2851.2	$(5.1 \pm 0.4) \times 10^{-24}$
773	725.8	$(1.3 \pm 0.2) \times 10^{-22}$
823	108.0	$(1.9 \pm 0.2) \times 10^{-21}$
873	8.64	$(1.1 \pm 0.2) \times 10^{-20}$
923	21.6	$(1.9 \pm 0.2) \times 10^{-19}$
974	3.6	$(1.4 \pm 0.2) \times 10^{-18}$
1023	2.7	$(1.1 \pm 0.2) \times 10^{-17}$
1081	0.36	$(9.1 \pm 0.7) \times 10^{-17}$
1143	0.27	$(3.3 \pm 0.2) \times 10^{-16}$
1153	0.27	$(4.1 \pm 0.6) \times 10^{-16}$

Fig. 2 Arrhenius plot for W diffusion in α-Fe, present work and Ref. [15]

The conversion of the energy spectra to diffusion profiles was made according to the algorithm developed in Ref. [14].

3 Results

The experimental setup was expected to be consistent with the thin-film solution of Fick's law, namely:

$$C(x) = \frac{M}{\sqrt{\pi D t}} \exp\left(\frac{-x^2}{4Dt}\right) \tag{3}$$

where C is the W concentration at depth x, M is the initial amount of W onto the sample surface, D is the diffusion coefficient at the studied temperature and t is the annealing time.

All the penetration profiles ($\ln[C(x)]$ against $(x)^2$) are displayed in Fig. 1. In all cases, straight lines were obtained, so that expression (3) is followed.

The diffusion coefficients obtained are listed in Table 3 together with temperatures and annealing times.

The corresponding Arrhenius plot is shown in Fig. 2, together with values obtained in a previous measurement [15] performed in a smaller temperature range. A departure from the Arrhenius law is observed, as expected; the results can be fitted by

$$D(T) = 2.3 \times 10^{-6}$$
$$\times \exp\left[-\frac{(215\,\text{kJ}\,\text{mol}^{-1}) \times (1 + 0.176s^2)}{RT}\right] \text{m}^2\,\text{s}^{-1} \tag{4}$$

where D_0^p and Q^p were obtained by fitting the last three points of Table 3 in the paramagnetic region with an Arrhenius law, and α by applying the ferromagnetic model for diffusion as discussed next.
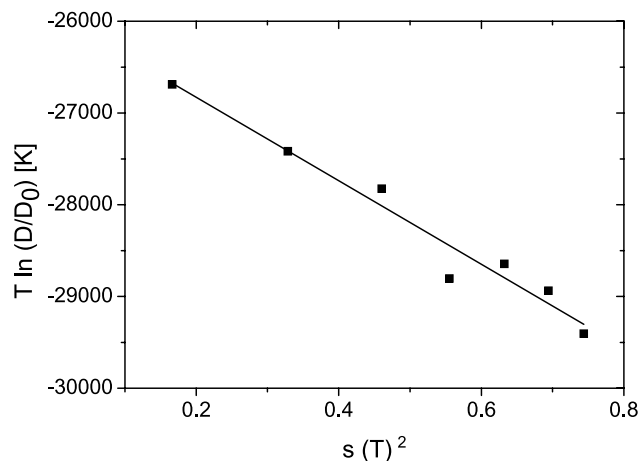
Fig. 3 Equation (5) applied to ferromagnetic data listed in Table 3

4 Discussion

First, in order to fit the measured data with the ferromagnetic model, let us note that (1) can be rewritten as

$$\left[T \ln\left(\frac{D(T)}{D_0^p} \right) \right] = -\frac{Q^p}{R} - \left(\frac{\alpha Q^p}{R} \right) s^2(T) \qquad (5)$$

Then, using the pre-exponential factor measured in the paramagnetic region it is possible to calculate the ferromagnetic fitting parameters from a least squares fit of the plot $T \ln(D/D_0^p)$ vs. s^2.

Such a plot is shown in Fig. 3; a good linear fit is obtained. From the slope, αQ^p equals 38 ± 4 kJ mol^{-1}, and from the intercept the activation energy in the paramagnetic region can be recalculated, $Q_{rec}^p = 215.5 \pm 2.0$ kJ mol^{-1}. The latter is in excellent agreement with the value determined by the diffusion coefficient measured in the paramagnetic region, $(215 \pm 20$ kJ mol$^{-1})$, thus proving the model's self-consistency. From these quantities a dimensionless α of 0.176 ± 0.02 is obtained.

Equation (1) means that below T_C the Fe spins begin to align, producing an increment in the activation energy due to the increase of lattice stiffness, which is proportional to the square of the spontaneous magnetization and takes its maximum value at 0 K.

The stiffness has two contributions; the first one is given by the interaction among the spins of the matrix Fe atoms. The second one is due to the interaction between the magnetic spin of the diffuser and the spins of the Fe atoms involved in the diffusion jump.

The first contribution is the same for all elements in the α-Fe matrix, the second contribution being responsible for the change in αQ^p from one diffuser to another. Then, when the diffuser is Co, with a magnetic moment higher than Fe, the increment in the activation energy is higher than for self-diffusion and, consistently, for Cr, which aligns anti-parallel

to the matrix and has a smaller magnetic moment, αQ^p is lower.

When the diffuser is a non-magnetic atom, like Sn, Sb, Nb or W, the second contribution is null, so that one can expect almost constant values for αQ^p, as effectively observed from the reported data in Table 1.

This idea is well supported by ab-initio calculations performed within the local spin density approximation (LSDA) [16] in order to get values for vacancy formation and migration energies in the paramagnetic state of bcc Fe (non-spin polarized calculations) and the ferromagnetic 0 K state (spin polarized).

The Arrhenius plot of Fig. 2 shows our measurements together with those of a previous work [15] for W diffusion in α-Fe performed in a shorter temperature range. As one can see the agreement between both sets of diffusion coefficients is quite good, in particular in the ferromagnetic region. Nevertheless the fitting diffusion parameters are rather different: $D_0^p = 1.5 10^{-2}$ m^2 s^{-1}, $Q^p = 287$ kJ mol^{-1} and $\alpha = 0.086$; consequently, the increment in the activation energy due to ferromagnetism is significantly lower $\alpha Q^p = 25$ kJ mol^{-1}.

The reason for such large differences in the diffusion parameters, being so similar the diffusion coefficients, lies in the very short temperature range of the paramagnetic region [1043–1184 K] in which the pre-exponential factor D_0^p is determined, combined with the exponential behaviour of the Arrhenius law.

In fact, several authors have measured diffusion of W in paramagnetic α-Fe, among them Gruzin [17], Kieszniewski [18] and Kučera et al. [19] using the β-ray emitter ^{185}W and the residual activity method, and Alberry and Haworth [20] using the diffusion couple method. Excluding Gruzin's measurements [17] and despite the differences among impurity content, grain size, and experimental techniques used, all the data in that region are superposed within the experimental error, see for instance Fig. 3 in [15]. Nevertheless, there is a large variation in the pre-exponential factor obtained, ranging from 10^{-2} to 10^{-6} m^2 s^{-1}.

Regarding the ferromagnetic region, one can merge the data reported in [15] with the present ones, and analyze the complete data set by applying (5), this is shown in Fig. 4. Figure 4(a) uses the D_0^p from [15], 1.5×10^{-2} m^2 s^{-1}, then a rather scattered behaviour is observed. In Fig. 4(b) our current value, 2.3×10^{-6} m^2 s^{-1}, is used instead and this time a nice linear behaviour is obtained.

Moreover, on the basis of Vineyard's harmonic transition-state theory [21, 22] D_0 can be calculated through a ratio between phonon frequencies. Calculation must be performed in two supercells with $N - 1$ atoms, one with the hopping atom at the saddle-point configuration and the other in the equilibrium (stable vacancy) configuration. Unusually high phonon frequencies for a metal are needed in order to achieve D_0^p as high as 10^{-2} m^2 s^{-1}, which is not generally obtained when such a kind of calculation is performed [23].

a Using D_0^p from [15].

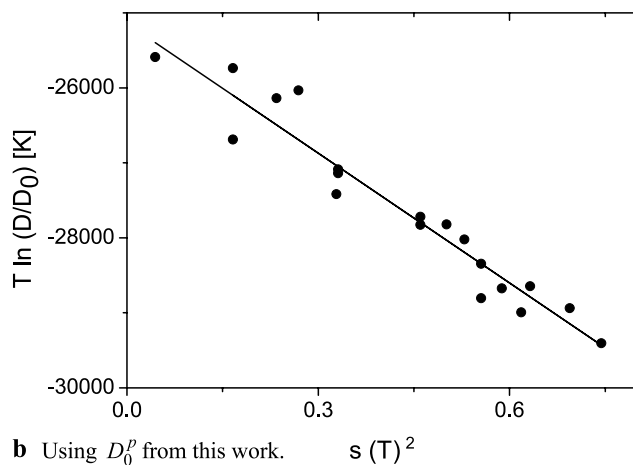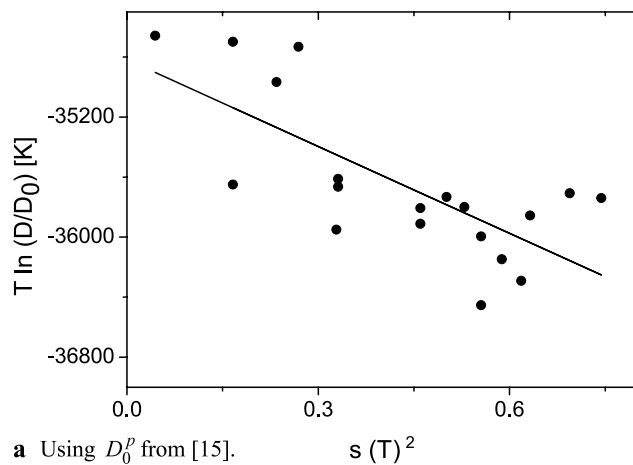**b** Using D_0^p from this work.

Fig. 4 Equation (5) applied to the ferromagnetic data from the present work together with the ones in Ref. [15]. (**a**) Using D_0^p from [15]. (**b**) Using D_0^p from this work

Diffusion in α-Fe matrices may depend on the impurity content (particularly C and O), the grain size, the level of surface stress, the dislocation density, etc.; so that studies performed in the same kind of samples, with the same annealing treatment and the same experimental technique, like in the present work, are necessary in order to establish a comparison of the behaviour. Only under such conditions can one show that non-magnetic substitutional diffusers are affected by the ferromagnetism in the same way, with a maximum increment in the activation energy equal (within experimental error) for all of them.

According to our experimental conditions, this increment is close to 40 kJ mol^{-1}, though the error, about 10%, stemming from simple statistical analysis of the data could be an underestimation. The strong variation in D_0^p due to a small variation in the diffusion coefficients measured in the paramagnetic region, introduces a higher error in the values of αQ^p, which can be estimated to be close to 50% after comparison of the present work with [15].

5 Conclusions

A study of W diffusion in ferro- and paramagnetic α-Fe was performed in an extended temperature range, from 723 to 1153 K.

A curvature in the Arrhenius plot was found, as usual for self- and substitutional diffusion in the matrix. The curvature is ascribed to the ferromagnetic effect on diffusion.

The application of a previous model for the diffusion of non-magnetic impurities in ferromagnetic α-Fe obtains an excellent fit to the experimental data.

A constant value for the total increment (at 0 K) of the activation energy due to ferromagnetism is found for all the non-magnetic substitutional diffusers measured in α-Fe. This behaviour is supported by theoretical calculations.

References

1. M. Lübbehusen, H. Mehrer, Acta Metall. Mater. **28**, 283 (1990)
2. K. Hirano, Y. Ijima, Defect Diffus. Forum **66–69**, 1039 (1989)
3. L.A. Girifalco, J. Phys. Chem. Solids **23**, 1171 (1962)
4. L. Ruch, D.R. Sain, H.L. Yeh, L.A. Girifalco, J. Phys. Chem. Solids **37**, 649 (1976)
5. J. Crangle, G.M. Goodman, Proc. R. Soc. Lond. A **321**, 477 (1971)
6. H. Mehrer, D. Höpfel, G. Hettich, in *DIMETA-82 Diffusion in Metals and Alloys*, ed. by F.J. Kedves, D. Beke, vol. 360 (Trans. Tech. Publications, Aedermannsdorf, 1983)
7. Y. Iijima, K. Kimura, C. Lee, K. Hirano, Mater. Trans., JIM **34**, 20 (1993)
8. C. Lee, Y. Iijima, T. Hiratani, K. Hirano, Mater. Trans., JIM **31**, 255 (1990)
9. J. Cermak, M. Lübbehusen, H. Mehrer, Z. Met.kd. **80**, 213 (1989)
10. R.A. Pérez, D.N. Torres, F. Dyment, Appl. Phys. A, Mater. Sci. Process. **97**(2), 381 (2009)
11. R.A. Pérez, Appl. Phys. A, Mater. Sci. Process. **92**(2), 325 (2008)
12. R.A. Pérez, D.N. Torres, M. Weissman, F. Dyment, Defect Diffus. Forum **194–199**, 97 (2001)
13. D. Torres, R.A. Pérez, F. Dyment, Acta Metall. Mater. **48**, 2925 (2000)
14. R.A. Pérez, G. García Bermúdez, F. Dyment, H. Somacal, D. Abriola, Defect Diffus. Forum **143–147**, 1335 (1997)
15. S. Takemoto, H. Nitta, Y. Iijima, Y. Yamazaki, Philos. Mag. **87**, 1619 (2007)
16. R.A. Pérez, M. Weissman, J. Phys., Condens. Matter **16**, 7033 (2004)
17. P.L. Gruzin, Dokl. Akad. Nauk SSSR **94**, 681 (1954)
18. J. Kieszniewski, Pr. Inst. Hut. **19**, 253 (1967)
19. J. Kučera, B. Million, K. Ciha, Kov. Mater. **7**, 9 (1969)
20. P.J. Alberry, C.W. Haworth, Met. Sci. **8**, 1269 (1974)
21. G.H. Vineyard, J. Phys. Chem. Solids **3**, 121 (1957)
22. P. Hänaggi, P. Talkner, M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990)
23. S. Huang, D. Worthington, M. Asta, V. Ozolins, G. Ghosh, P. Liaw, Acta Mater. **58**, 1982 (2010)