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Diffusion in iron-arsenic alloys

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The distribution of arsenic in various diffusion couples of high purity iron–arsenic alloys (0.6 to 4.6 at. % As) was measured by a micro-probe analyser, following a diffusion annealing treatment at 950 to 1380° C. The results show that the temperature dependence of the diffusion coefficient of arsenic in α- and γ-iron may be represented by the following equations:

$$D_\alpha = 4.3 \exp(-52\,500/RT)\ \text{cm}^2\ \text{sec}^{-1}$$

$$D_\gamma = 0.58 \exp(-58\,900/RT)\ \text{cm}^2\ \text{sec}^{-1}$$

1. Introduction

When the solvent element belongs to the group of transition elements, the activation energy for diffusion of a transition element differs very little from that for self-diffusion of a solvent [1]. However, the difference may become considerable, i.e. up to 20%, when a non-metallic solute element is diffusing. The temperature dependence for the diffusion coefficient of arsenic in γ-iron has been given by:

$$D_\gamma = 0.16 \exp(-58\,600/RT)\ \text{cm}^2\ \text{sec}^{-1}.$$

Kudryavtseva *et al.* [2] studied the diffusion of arsenic in low-carbon steel within the range 900 to 1200° C. The diffusion involved net flow arsenic atoms from the liquid solution (30.5 at.% As) into solid steel specimens (0 to 0.78 at.% As). During the diffusion annealing, the γ-phase of the specimens was transformed into α-phase, when the former reached saturated arsenic concentration. Prior to diffusion annealing, the first specimens were either heated to an elevated temperature of 1250° C, followed by water-quenching or used in the annealed state. The latter had the highest value of activation energy: 59 000 cal g-atom^{-1} for γ-iron and 50 600 cal g-atom^{-1} for α-iron. The quenched specimens had the lowest value of activation energy: 34 000 cal g-atom^{-1} for γ-iron and 29 800 cal g-atom^{-1} for α-iron. Thus quenching increases the concentration of defects in the crystal lattice and, consequently, accelerates arsenic diffusion.

It was reported that the diffusion coefficient for arsenic in iron is $D_\alpha = 7.9 \times 10^{-11}\ \text{cm}^2\ \text{sec}^{-1}$ and $D_\gamma = 8.9 \times 10^{-10}\ \text{cm}^2\ \text{sec}^{-1}$ at 800 and 1150° C, respectively [3].

Krass [4] has determined that the diffusion coefficient of arsenic in steel at 1000° C is $D = 2.27 \times 10^{-9}\ \text{cm}^2\ \text{sec}^{-1}$. The diffusion mobility of arsenic coincides with that of phosphorus.

Predel and Frebel [5] have stated that the activation energy of arsenic diffusion in α-solid solution of iron–arsenic has the value:

$$Q_\alpha = 38\,000\ \text{cal g-atom}^{-1}.$$

In the literature available [6] no particular attention has been devoted to the diffusion mobility of arsenic in iron. The given data were mainly related to industrial iron alloys. In most cases there was a shortage of detailed information concerning investigation methods. Therefore, the purpose of this study is the determination of the diffusion coefficient of arsenic using high purity iron–arsenic alloys.

2. Experimental method

The iron–arsenic alloys used in this study were made from carbonyl-iron ($C < 7$ ppm, $O < 100$ ppm, $S < 1$ ppm) and metallic arsenic (99.9%As). Melting was carried out in a beryllia crucible in an argon atmosphere. The as-cast material was machined into specimens 9 mm in diameter and 5.0 mm in length.

In order to obtain a large grain size and eliminate dendritic segregation, all specimens were annealed in evacuated quartz tubes (10^{-4} mm Hg) at temperatures 50 to 250° C higher (Table I) than those selected for diffusion experiments. Following annealing, the specimens were cooled at an average rate of $1.0°\,C\,min^{-1}$.

The treatment described yielded alloys free of dendritic segregation (as revealed by Stead's reagent) and with a grain size approximately 2 mm in diameter.

Diffusion welding was carried out at 800° C for 1 h on couples firmly clamped (1.5 kgf m) in a thick-wall device made of stainless steel. The technique proved to give a good contact with no measurable diffusion of arsenic in the vicinity of the seam.

The compositions of the diffusion couples used in this study and the corresponding annealing temperatures are shown in Fig. 1, on part of the Fe–As equilibrium diagram [7]. The end points of the broken horizontal lines represent the As concentration in a given couple.

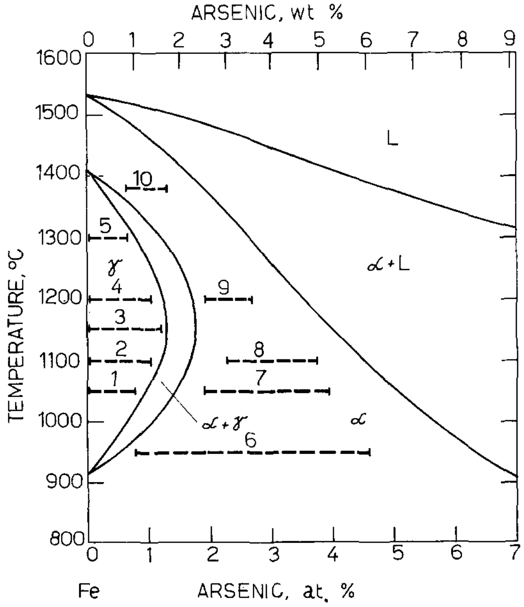

Figure 1 Part of the Fe–As equilibrium diagram.

Diffusion annealing was carried out in a tube furnace controlled to within ±2° C. The diffusion couples, sealed in evacuated quartz tubes, were heated to a given temperature, annealed for various periods of time (Table I) and quenched into a 10% NaCl solution. Heating and cooling were estimated to have taken not more than 1.5% of the complete anneal.

Following diffusion annealing, the couples were ground perpendicular to the welding seam, and slightly etched by Dickenson's reagent.

The distribution of arsenic, in the diffusion zone, was measured by a JEOL-JXA-3 A micro-probe analyser, at an accelerating voltage of 20 kV. Scans were made perpendicular to the weld of the diffusion couples, counting X-ray quanta for fixed periods of time (up to 100 sec), at a series of points along the line of scan. The size of the area sampled and the spacing of point analyses was 340 to 1550 μm and 10 to 220 μm, respectively, the former depending on the diffusion couples, and the latter on the distance from their welds (Fig. 3). The micro-probe was calibrated using annealed specimens of known composition. At least four calibrations per diffusion curve were carried out using specimens with a composition as close as possible to the measured concentration. No theoretical corrections were made. The calibration was completely empirical. The content of arsenic was determined to within an accuracy of 1 to 6%.

A typical concentration-distance curve is shown in Fig. 2.

3. Results

The well-known Matano method [8] was used to establish, if it exists, the dependence of the diffusion coefficient on the concentration of the

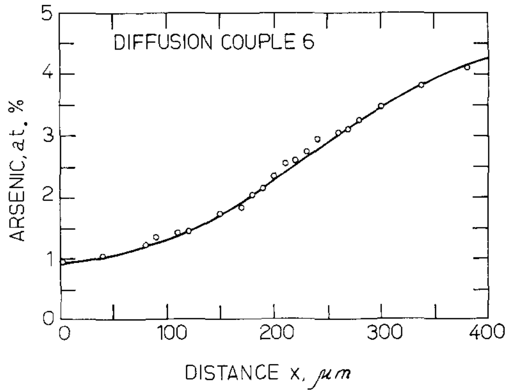

Figure 2 Concentration–distance curve. Diffusion time is 4.152 sec.

alloying element. However, the results failed to reveal any reliable dependence of the diffusion coefficient on arsenic content, i.e. variation of the diffusion coefficient with arsenic concentration at various diffusion couples showed negligible and random dependence (Fig. 3). Consequently, the diffusion coefficient was assumed to be virtually independent of the concentration, and Fick's second law, in the following form:

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

was used in subsequent calculations. Here $c(x, t) = c$, is the concentration of arsenic at a distance (x), from the weld interface perpendicular to the diffusion front, after a given period of time (t).

In the boundary conditions:

$$c(x, t) = c_2 \text{ for } x > x_0 \text{ at } t = 0$$

$$c(x, t) = c_1 \text{ for } x < x_0 \text{ at } t = 0,$$

the solution of the diffusion equation (Equation 1) has the form:

$$2\frac{c(x, t) - c_1}{c_2 - c_1} - 1 = \operatorname{erf}\left[\frac{x - x_0}{2\sqrt{Dt}}\right]. \tag{2}$$

This equation represents a straight line on the probability paper.

The results are summarized for more diffusion couples in Fig. 3. These, as well as subsequent calculations, were estimated by the least squares method. In all cases, a linear relationship was obtained. On the basis of the data derived from Fig. 3, the values of the error function and the diffusion coefficients were determined. The diffusion coefficients are summarized in Table I, together with other relevant data.

TABLE I Times and temperatures of diffusion annealing and diffusion coefficients of As in α- and γ-iron.

Temperature (° C)	$10^4/T$ (K^{-1})	Diffusion time $\times 10^{-4}$ (sec)	$D_\alpha \times 10^8$ (cm^2 sec^{-1})	$D_\gamma \times 10^{10}$ (cm^2 sec^{-1})
950	8.18	4.152	0.19	–
1050	7.56	15.066	1.04	0.88
1100	7.28	8.310	2.09	2.66
1150	7.03	3.648	–	5.62
1200	6.79	2.262	3.72	12.50
1300	6.36	0.774	–	31.20
1380	6.05	0.366	66.20	–

The activation energies and frequency factors were calculated from the slope and interception of $\ln D$ versus $1/T$ plot, respectively (Fig. 4). Equations for the diffusion coefficients of As in α- and γ-iron are as follows:

$$D_\alpha = 4.3 \exp(-52\,500/RT) \text{ cm}^2 \text{ sec}^{-1}$$

$$D_\gamma = 0.58 \exp(-58\,900/RT) \text{ cm}^2 \text{ sec}^{-1}.$$

4. Discussion

The diffusion coefficients and the activation energies determined in this study agree reasonably well with the previously published data [1–3] (Fig. 4). The diffusion coefficient in the work of Krass [4] and its value in this research are not compared, because it was not shown to which phase of iron the diffusion coefficient of the previous work pertains. It is probable that owing to the various heat-treatments of the starting materials used in the diffusion experiments, a difference exists between the activation energy obtained in this study and that in [5].

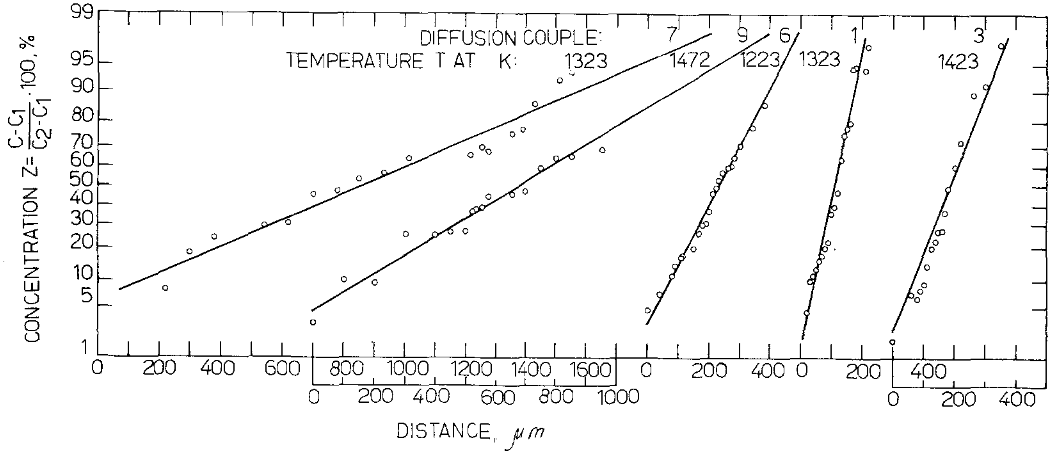

Figure 3 Some concentration–distance curves plotted on probability paper. Diffusion times are 15.066, 2.262, 4.152, 15.066 and 3.648 sec for diffusion couples 7, 9, 6, 1 and 3, respectively.

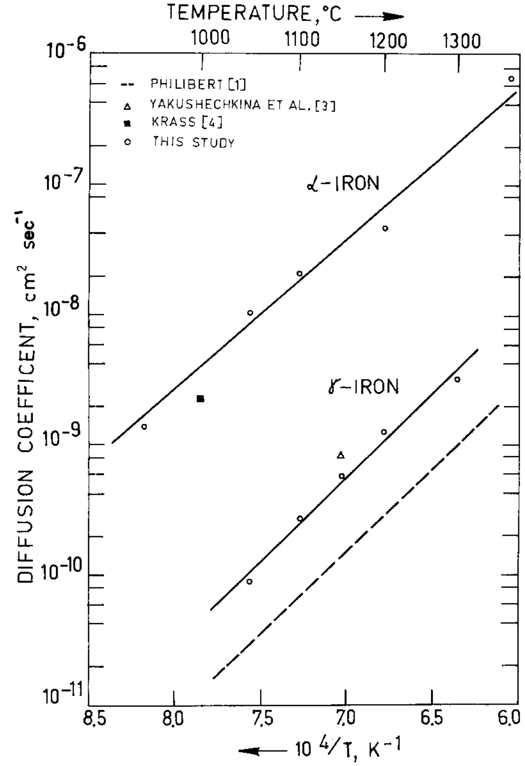

Figure 4 Temperature dependence of the diffusion coefficient.

The energy of movement of a solute ion from a normal lattice site into the saddle-point position adjacent to the vacant site was calculated by Swalin [9] on the basis of the elasticity theory. The solute ion is considered as an elastic sphere, and thus the enthalpy of jumping, ΔH_2, is the result of a two-dimensional hydrostatic compression of the solute ion of Goldschmidt radius r_0' to r_a and, due to dilation the saddle-point constriction, from r_h to r_a. An equation was derived on the basis of this model which permits calculation of the activation energy for solute diffusion in terms of the bulk modulus of the solute ion, B_s and solvent, B. The activation energy of diffusion:

$$Q = \Delta H_1 + \Delta H_2 \tag{3}$$

where ΔH_1 represents the enthalpy of vacancy formation for self-diffusion of the solvent which is equal to about $0.6Q$, and thus Q for a fcc lattice is given by:

$$Q = 0.6\,Q_{\text{self}} + \frac{0.344(r_0' + r)^2 r_0' B_s k_2 N}{\left[1 + \dfrac{12\pi B_s r_0' k_2}{(\sqrt{3}\,r_0' - 0.27\,r_0)\,C\,k_1}\right]} \tag{4}$$

where r = radius of a solvent ion, C = effective shear modulus of solvent related to the elastic constants C_{44}, C_{12} and C_{11} by the relationship $C = C_{44} + \frac{1}{2}(C_{11} - C_{12})$, N = Avogadro's number, k_1 and k_2 = geometrical constants.

Using Swalin's model, Krishtal and Mokrov [10] calculated a similar equation for a bcc lattice which, with the approximations accepted in [9], takes the form:

$$Q = 0.6\,Q_{\text{self}} + \frac{0.524(r_0' + r)^2 r_0' B_s k_2 N}{\left[1 + \dfrac{36\pi r_0' B_s k_2}{(4\sqrt{2}\,r_0' - 0.344r)\,C k_1}\right]} \tag{5}$$

Equation 5 is comprised of the same terms as Equation 4 but has other numerical coefficients.

The activation energies for the diffusion of different substitutional elements, in α- and γ-iron were calculated by Krishtal and Mokrov [10] according to Equations 4 and 5. The results showed reasonable agreement with the experimental data, in all but two instances, i.e. for diffusion of chromium and cobalt.

A similar approach was adopted in this study to calculate the activation energy for arsenic diffusion in α- and γ-iron. The relevant numerical data are summarized in Table II. The experimental Q_{exp}, and the calculated activation energies, Q_{theor}, are presented in Table III.

TABLE II Numerical data used in the calculation of activation energies

Parameter	α-iron	γ-iron	Reference
k_1	5.66*	13.3	[9]
k_2	2.08*	3.74	[9]
r (Å)	1.24	1.26	
r_0' (Å)	1.27	1.28	
Q_{self}(cal g-atom^{-1})	59.700	67.000	[11]
$C \times 10^{-4}$ (cal cm^{-3})	3.84		
$B_{\text{Fe}} \times 10^{-4}$ (cal cm^{-3})	3.98		[12]
$B_s \times 10^{-4}$ (cal cm^{-3})	0.433†		
r_0 (Å)	1.48		[2]

*Relevant data used to calculate k_1 and k_2 for α-iron was taken from [10].

†Calculated according to $B_s \cong 0.87\ B_{\text{exp}}$ [13], where B_{exp} is the experimental bulk modulus of pure arsenic.

TABLE III Activation energies

Phase	Q_{exp}(cal g-atom^{-1})	Q_{theor}(cal g-atom^{-1})
α-iron	52 500	47 900
γ-iron	58 900	55 400

In spite of a number of approximations used in the diffusion model quoted, the correlation between the experimental and theoretical values determined in this work is very good. This may be taken to indicate that the essential factor controlling the diffusion of arsenic in α- and γ-iron is its great compressibility, which is 8 times greater than that of iron.

According to [14, 15] a somewhat lower theoretical value may arise from an electronegative factor not being used in the proposed elastic diffusion model.

Finally, we must emphasize that there have been recent attempts to estimate the activation energy of diffusion, using modified elastic models and alternative approaches [16–18].

6. Conclusion

The experimentally determined equations for the diffusion coefficients of arsenic in γ- and α-iron are as follows:

$$D_\gamma = 0.58 \exp(-58\,900/RT)\ \text{cm}^2\ \text{sec}^{-1}$$

$$D_\alpha = 4.3 \exp(-52\,500/RT)\ \text{cm}^2\ \text{sec}^{-1}$$

The experimentally determined activation energies agree reasonably well with the theoretical values. This may be taken to indicate that the essential factor controlling the diffusion of arsenic in iron is its great compressibility. Accordingly, the activation energy for arsenic diffusion is smaller than for the self-diffusion of iron.

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References

1. J. PHILIBERT, *Traitement Thermique* **53** (1970) 27.
2. L. N. KUDRYAVTSEVA *et al.*, *Met. i Gornorudn. Prom. Nauchno-Tech. i Proizv. Sb.* **2** (1972) 34.
3. L. I. YAKUSHECHKINA *et al.*, *Izvest. V.U.Z. Chernaya Met.* **4** (1974) 116.
4. W. KRASS, *Neue Hütte* **14** (1969) 247.
5. B. PREDEL and M. FREBEL, *Arch. Eisenhüttenw.* 42 (1971) 365.
6. "Diffusion and Defect Data", 1967 to 1974 (Diffusion Information Center, Cleveland, Ohio).
7. V. N. SVECHNIKOV and A. K. SHURIN, *Sb. Voprosy Fiziki Metallov i Metallovedeñya, AN USSR* 7 (1957) 51.
8. W. SEITH and Th. HEUMANN, "Diffusion in Metallen". (Springer-Verlag, Berlin, 1955) p. 97.
9. R. A. SWALIN, *Acta Met.* **5** (1957) 443.
10. M. A. KRISHTAL and A. P. MOKROV, *Fiz. Met. Metallov.* **15** (1963) 456.
11. M. A. KRISHTAL, Mekhanizm Diffuzii v Zheleznykh "Splavakh" (Metallurgiya, Moskva, 1972) p. 296.
12. M. A. KRISHTAL, *ibid*, p. 321.
13. B. L. AVERBACH *et al. Acta Met.* **2** (1954) 92.
14. W. HUME-ROTHERY, "The Structures of Alloys of Iron", (Pergamon Press, Oxford, 1963) p. 88.
15. P. G. SCHEWMON, "Diffusion in Solids", (McGraw-Hill, New York, 1963) p. 96.
16. C. P. FLYNN, *Phys. Rev.* **171** (1968) 682.
17. *Idem*, "Point Defects and Diffusion" (Clarendon Press, Oxford, 1972).
18. R. A. JOHNSON, in "Diffusion in Body Centred Cubic Metals" (A.S.M., Cleveland, Ohio, 1965).

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