JOURNAL OF MATERIALS SCIENCE 4 (1969) 797–801

The Determination of the Diffusion Constants of Oxygen in Nickel and α-Iron by an Internal Oxidation Method

R. BARLOW, P. J. GRUNDY
Department of Pure and Applied Physics, University of Salford, Lancs, UK

Received 1 May 1969

The diffusion constants of oxygen in nickel and α-iron are calculated from experimentally determined internal oxidation rates in dilute silicon-bearing alloys. A single crystal alloy of composition 0.058 wt % silicon in nickel and polycrystalline alloys of composition 0.48 wt % silicon in nickel and 0.072 wt % silicon in iron were oxidised and allowance is made for the absorption of oxygen in the reaction with silicon. For nickel the values of activation energy $Q = 73.9$ kcal/g atom in the range 800 to 1200° C and $Q = 74.4$ kcal/g atom in the range 900 to 1300° C are in good agreement with a previous result. The activation energy required for oxygen diffusion in α-iron was found to be 39.9 kcal/g atom in the range 700 to 850° C.

1. Introduction

There have been few determinations of the diffusion constants of oxygen in nickel reported in the literature. The results of Goto *et al* [1], appear to be the only recently published values for the temperature range of interest, i.e. 800 to 1300° C. Smithells and Ransley [2] give a value for the activation energy for diffusion and values of the diffusion coefficient in the temperature range 900 to 1050° C but, as pointed out by Meijering and Druyvesteyn [3], these values are probably in error. The diffusion constants have been measured in a lower temperature range (680 to 830° C) by Messner *et al* [4]. No data on the diffusion constants of oxygen in α-iron can be found in the literature.

The experimental technique used to measure the diffusion constants is the same as that used by Goto *et al*, namely exclusive* internal oxidation. The measurements reported here form part of an investigation into the structure and magnetic properties of internally oxidised ferromagnetic alloys. Internal oxidation provides diffusion data on oxygen that can be applied to the pure metal because the oxidation is diffusion-controlled [5], i.e. the diffusion of both the interstitial oxygen and the reacting substitutional solute is governed by normal diffusion equations of the form

$$D = D_c \, e^{-Q/RT} .$$

The precipitated oxide acts as a marker and at sufficiently small concentrations of the solute the effect of the well dispersed oxide product on the diffusion of oxygen is negligible. When account is taken of the absorption of oxygen by the solute, values of the diffusion constants of oxygen in the base metal are obtained.

2. The Rate of Internal Oxidation

If a dilute alloy, in which the solute has a greater affinity for oxygen than the solvent, is heated in an oxidising atmosphere, oxygen may diffuse into the alloy, react with the solute and cause a solute oxide to be precipitated in the parent matrix. This process is called *internal oxidation.*

It is assumed that the distribution of dissolved oxygen and dissolved alloying element at some stage in the internal oxidation of a dilute alloy can be represented by fig. 1. The oxygen is supplied to the outside surface at a sufficient rate to maintain saturation of the base metal, and diffusion inwards occurs along the concentration gradient C_0–C_X. Upon precipitation of the solute

---

*"Exclusive" means that only the solute is oxidised.

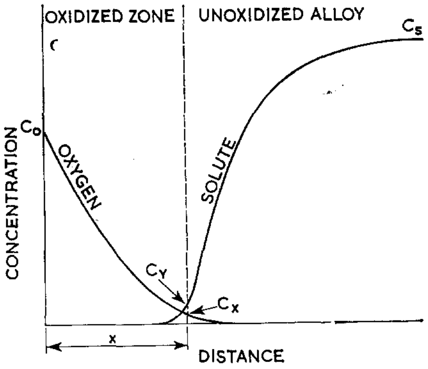

Figure 1 Ideal distribution of dissolved oxygen and solute element during the internal oxidation process.

oxide, a solute concentration gradient is produced and the form of this gradient is governed by the relative diffusion rates of oxygen and solute in the base metal [5].

The growth of the oxidised zone in dilute alloys has been shown [6, 7] to follow a relation of the form

$$X^2 \propto t \tag{1}$$

where X is the depth of penetration of the oxidised zone and t is the time of oxidation. This time is also dependent upon the temperature of oxidation T as

$$t \propto e^{Q/RT} \tag{2}$$

where Q is an activation energy. Thus the growth rate of the internally oxidised zone can be expressed in the form of the well known diffusion law as

$$\frac{X^2}{t} = D_c\, e^{-Q/RT} \tag{3}$$

where D_c is a constant of proportionality.

By a derivation based on Fick's law, Rhines [6] showed that the time-dependence of the growth of the internally oxidised zone at constant temperature can be expressed as

$$\frac{X^2}{t} = \frac{2C_O D_O - 1.68\,\frac{O}{S}\,C_S D_S}{\frac{O}{S}\,C_S + \frac{C_O}{3}} \tag{4}$$

if the oxygen and solute concentration at the oxidation front, C_X and C_Y respectively, are assumed to be zero. Here D_O and D_S are the diffusion coefficients of oxygen and solute respectively, C_O is the oxygen concentration at the solubility limit, C_S is the original alloy concentration and O/S is the weight ratio of oxygen to metal in the oxide precipitated.

The equation is expected to hold to within 1% as long as

$$\frac{D_O C_O\, S}{D_S C_S\, O} \geqslant 5 \tag{5}$$

3. Experimental Procedure

The single crystal alloy (Ni–0.058 wt % Si) was grown by Metals Research Limited from 5 N purity materials whilst the polycrystalline alloys used were prepared from Johnson Matthey Limited spectroscopically pure nickel, iron and silicon.

Discs of 3 mm diameter and thickness ~ 500 μm, obtained by spark-machining, were internally oxidised for various times and at several temperatures in a "Rhines pack" [8] in a closed silica tube. In this "Rhines pack" the partial pressure of oxygen is maintained at the dissociation pressure of the lowest oxide of the base metal so that only the oxide of the less noble solute element can be formed. For the nickel alloys the pack was composed of NiO–Ni_2O_3, Ni and Al_2O_3 powders in the ratio 2:1:1 and for the iron alloy Fe_2O_3, Fe and Al_2O_3 powders in the same ratio.

The penetration depth of the oxidation front was measured using an optical microscope after the discs had been embedded in a plastic material, sectioned, mechanically polished and finally electropolished (nickel alloys) or etched in 5% nitric acid-ethanol solution (iron alloy).

4. Results

4.1. Nickel

As previously reported [7], penetration depths of the internal oxidation front, in a *single crystal* Ni–0.058 wt % Si alloy, have been measured for varying oxidation times and at several temperatures in the range 800 to 1200° C. It was found that equation 3 expressed the temperature-dependence of the penetration rate of the oxidation front. Consideration of equation 3 shows that X^2/t, the penetration rate, may be considered as the "diffusion coefficient" (D_{ox}) of the oxidation front. The constants $(D_c)_{ox}$ and $(Q)_{ox}$ for this alloy were computed from a plot of $\ln X^2/t$ against $1/T$ by the method of least squares as $9.7 \pm 1.0 \times 10^3$ cm²/sec and 70.9 ± 2.3 kcal/g atom respectively (table I).

TABLE I Experimentally and theoretically determined internal oxidation constants for the Ni–Si alloys considered.

	Alloy	Temperature range	$(D_c)_{ox}$ cm²/sec	$(Q)_{ox}$ kcal/g atom
Experimental	Ni–0.058 wt % Si	800–1200° C	$9.67 \pm 0.95 \times 10^3$	$70.9_1 \pm 2.28$
Experimental	Ni–0.48 wt % Si	900–1300° C	$1.51 \pm 0.07 \times 10^3$	$71.5_6 \pm 0.88$
Theoretical	Ni–0.48 wt % Si	900–1300° C	$1.46 \pm 0.03 \times 10^3$	$71.5_1 \pm 0.37$
Experimental	Ni–0.77 wt % Si	1000–1300° C	$1.86 \pm 0.13 \times 10^3$	$73.2_7 \pm 1.50$
Theoretical	Ni–0.77 wt % Si	1000–1300° C	$1.70 \pm 0.04 \times 10^3$	$73.4_0 \pm 0.84$

Values of D_{ox} calculated using these results can then be substituted, together with appropriate values for the other constants, into equation 4 to give values of the diffusion coefficient of oxygen in nickel, D_O, at several temperatures in the range 800 to 1200° C. The values of C_O used in these calculations were those abstracted by Smithells [9] while values of D_S were calculated from data given by Swalin *et al* [10]. It is probable that the C_O values used were the main source of error in the calculation because of interpolation at certain temperatures. The temperature-dependence of the diffusion coefficient D_O of interstitial oxygen in nickel is given by a normal diffusion equation, so that D_c and Q can finally be computed from a plot of ln D_O against $1/T$. The values so obtained are $D_c = 7.9 \pm 0.1 \times 10^4$ cm²/sec and $Q = 73.9 \pm 0.5$ kcal/g atom (table II).

A similar calculation applied to the penetration rate measurements made on a *polycrystalline* Ni–0.48 wt % Si alloy gives $D_c = 9.5 \pm 0.1 \times 10^4$ cm²/sec and $Q = 74.4 \pm 0.3$ kcal/g atom (table II).

The accuracy of equation 4 when applied to nickel-silicon alloys can be checked by substitution into the inequality 5. It is found that the inequality holds at 800° C provided $C_S \leqslant 0.57$ wt % and at 1200° C provided $C_S \leqslant 1.75$ wt %.

The oxidation constants of the Ni–0.48 wt % Si alloy and a polycrystalline Ni–0.77 wt % Si alloy have been determined experimentally and theoretically, (using the Rhines equation, 4), the results being shown in table I.* It can be seen that there is good agreement in both cases between the experimental and calculated values which shows that equation 4 is accurate to within 1 % at these low alloy concentrations. The oxidation front penetration rate in the Ni–0.77 wt % Si was little different from that in the Ni–0.48 wt % Si alloy, although occasionally the oxidation product acts as a barrier to the diffusing oxygen, making the penetration depth measurements more inaccurate. The precipitated oxide structure in the Ni–0.77 wt % Si alloy was similar to that in the Ni–0.48 wt % Si, being mainly filamentary in the grains and a continuous film in the grain-boundaries [7], and it is this

TABLE II Diffusion constants for oxygen in nickel calculated from measurements on (a) a single crystal Ni–0.058 wt % Si alloy (b) a polycrystalline Ni–0.48 wt % Si alloy.

	Temperature ° C	D_O cm²/sec	D_c cm²/sec	Q kcal/g atom
(a) Ni–0.058 wt % Si	800	8.38×10^{-11}		
	850	4.38×10^{-10}		
	925	3.19×10^{-9}		
	1000	1.78×10^{-8}		
	1075	9.99×10^{-8}		
	1150	4.19×10^{-7}		
	1200	1.00×10^{-6}		
	800–1200		$7.9 \pm 0.1 \times 10^4$	73.9 ± 0.5
(b) Ni–0.48 wt % Si	925	3.17×10^{-9}		
	1000	2.00×10^{-8}		
	1075	1.01×10^{-7}		
	1150	4.29×10^{-7}		
	1200	1.03×10^{-6}		
	1250	2.33×10^{-6}		
	1300	4.91×10^{-6}		
	900–1300		$9.5 \pm 0.1 \times 10^4$	74.4 ± 0.3

---

*The theoretical determination was made by substituting the appropriate value of D_O, as determined from the 0.058 wt % Si single crystal alloy, into equation 4 for the 0.48 wt % or 0.77 wt % alloy.

grain-boundary precipitation that produces the barrier to diffusing oxygen.

4.2. Iron

The penetration depths of the internal oxidation front were measured in a polycrystalline Fe–0.072 wt % Si alloy for varying oxidation times and at several temperatures in the range 700 to 850° C. The temperature range is limited because below 700° C the oxidation rate is extremely slow, while above 850° C enhanced grain-boundary precipitation begins to take place, causing uncertainty in the penetration depth measurements, The constants $(D_C)_{OX}$ and $(Q)_{OX}$ were computed from a plot of ln X^2/t against $1/T$ by the method of least squares as 90 ± 20 cm²/sec and 53.6 ± 2.5 kcal/g atom respectively. Unfortunately values of D_S in α-iron in the temperature range considered cannot be found in the literature. However, the diffusion coefficients of substitutional alloying elements are consistently two orders of magnitude less than those of the interstitial oxygen, so that the Rhines equation can be modified for use on iron alloys without the introduction of any appreciable error. The equation thus becomes.

$$D_O = \frac{X^2}{t}\left(\frac{1}{2}\frac{C_S}{C_O}\frac{O}{S} + \frac{1}{6}\right).$$

Several values of X^2/t and C_O can then be substituted to give values of the diffusion coefficient of oxygen D_O in α-iron in the temperature range 700 to 850° C. The values of X^2/t used in these calculations were determined by using the $(D_C)_{OX}$ and $(Q)_{OX}$ values given above, while the values of C_O were those given by Seybolt [11]. The values of D_O so calculated are shown in table III.

TABLE III Diffusion constants for oxygen in α-iron calculated from measurements on a polycrystalline 0.072 wt % Si-Fe Alloy.

Temperature °C	D_O cm²/sec	D_C cm²/sec	Q kcal/g atom
700	5.26×10^{-10}		
725	8.97×10^{-10}		
750	1.37×10^{-9}		
775	2.28×10^{-9}		
800	3.40×10^{-9}		
825	5.28×10^{-9}		
850	7.67×10^{-9}		
700–850		0.4 ± 0.1	39.9 ± 0.3

The temperature dependence of the diffusion coefficient of interstitial oxygen is given by the normal diffusion equation, so that the constants D_C and Q can be computed from a plot of ln D_O against $1/T$. This computation yields the results $D_C = 0.4 \pm 0.1$ cm²/sec and $Q = 39.9 \pm 0.3$ kcal/g atom. The sizeable difference between the activation energy values for the alloy and pure metal is a result of the large increase in oxygen solubility in the temperature range considered. In fact the solubility increases by a factor of 3, being 0.008 wt % at 700° C and 0.023 wt % at 850° C. Equation 5 should hold to within 1 % for the iron alloy in the temperature range considered, provided that $D_O/D_S \geqslant 50$. The value of D_S is unknown, but this ratio governs the dispersion of the oxide product, and electron microscopy has shown that the degree of dispersion of the oxide in the iron alloy is similar to that obtained in the most dilute nickel alloy where $D_O/D_S \sim 650$. Thus it can be assumed that equation 5 is applicable to the iron alloy considered here.

5. Discussion

The determined values of activation energy Q for interstitial oxygen diffusion in nickel are in reasonable agreement with the value given by Goto, i.e. 73.9 and 74.4 compared to 72.0 kcal/g atom. However our diffusion coefficients D_O in the temperature range 900 to 1300° C are consistently a factor of three higher than those of Goto. An explanation of this could be found in the fact that he used nickel-chromium alloys with a large solute content, ~0.6 to 4.0 wt %. It is probable that at these concentrations the precipitated oxide will have an impeding effect on the diffusing oxygen, thus reducing the diffusion coefficient D_O. The difference in the activation energies determined here is within the experimental error, while the values of D_C are such that calculation of the diffusion coefficient D_O with both sets of data gives results which are in excellent agreement. Comparison of the D_O values in table II shows the order of this agreement.

The values of the diffusion coefficient D_O in α-iron shown in table III are consistently a factor of four higher than those given by Schenck *et al* [12]. The experimental technique use by Schenck *et al* to determine the diffusion coefficients was the same as that used in this work, namely exclusive internal oxidation of dilute Si–Fe alloys, but the alloy concentration was never less than 0.24 wt % Si. The difference in alloy concentration used in the determinations may account for the difference in diffusion coefficients obtained. The alloy activation energy determined here is in reasonable agreement with values given by Schenck *et al* [12].

Acknowledgement

Acknowledgements are due to the SRC for the award of a Research Studentship (R.B.) and to the Air Force Office of Scientific Research for support through the European Office of Aerospace Research, OAR United States Air Force under Grant EOOAR-68-005.

References

1. S. GOTO, K. NOMAKI, and S. KODA, *J. Japan Inst. Met.* **31** (1967) 600.
   (Abstracted from *Diffusion Data* **1** (1967) 39.)
2. C. J. SMITHELLS and C. E. RANSLEY, *Proc. Roy. Soc.* **A155** (1936) 195.
3. J. S. MEIJERING and M. J. DRUYVESTEYN, *Philips Res. Rep.* **2** (1947) 81.
4. A. MESSNER, R. BENSON, and J. E. DORN, *Trans. ASM* **53** (1961) 227.
5. R. A. RAPP, *Corrosion* **21** (1965) 382.
6. F. N. RHINES, W. A. JOHNSON, and W. A. ANDERSON, *Trans. AIME* Tech. Publ. No. 1382 (1941).
7. R. BARLOW, P. J. GRUNDY, and B. JOHNSON, *J. Materials Sci.* **4** (1969) 352.
8. F. N. RHINES, *Trans. AIME* **137** (1940) 246.
9. C. J. SMITHELLS, "Metals Ref. Book" (Butterworths, London, 1967) p. 631.
10. R. A. SWALIN, A. MARTIN, and R. OLSON, *J. Metals Trans. AIME* **207** (1957) 936.
11. A. U. SEYBOLT, *J. Metals Trans. AIME* **6** (1954) 641.
12. H. SCHENCK, E. SCHMIDTMANN, and H. MÜLLER, *Arch. Eisenhüttenw.* **31** (1960) 121.