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Chemical volume diffusion coefficients for stainless steel corrosion studies

P. I. WILLIAMS*, R. G. FAULKNER
Loughborough University of Technology, UK

Chemical diffusion coefficients for chromium in austenitic and ferritic steels are determined using diffusion couples studied by electron probe microanalysis techniques. The average chemical volume diffusion coefficient, for the composition range 14 to 28 at% chromium, for ferritic AISI 446 in the temperature range 800 to 1000° C is:

$$\tilde{D} = 0.15\left(\begin{matrix}+0.54\\-0.12\end{matrix}\right)\exp\left(\frac{-210(\pm 15)}{RT}\right)\ \mathrm{cm^2\,sec^{-1}}$$

and for austenitic AISI 310 in the temperature range 800 to 1200° C is:

$$\tilde{D} = 0.27\left(\begin{matrix}+1.04\\-0.22\end{matrix}\right)\exp\left(\frac{-246(\pm 16)}{RT}\right)\ \mathrm{cm^2\,sec^{-1}}$$

where R is in kJ $\mathrm{K^{-1}\,mol^{-1}}$. Good agreement is found with existing data for ferritic steels but the data are more scattered in the austenitic case. Diffusion data from diffusion couples are thought to be more realistic than those obtained from tracer work for the purpose of predicting diffusion-controlled corrosion behaviour.

1. Introduction

Alloy diffusion can play an important role in many industrial processes. For example, during the corrosion of stainless steels the rate at which chromium can diffuse to the alloy surface can determine the protective nature of scales formed and hence metal wastage rates. The diffusion data reported here were measured during a study of the influence of alloy diffusion processes on corrosion [1]. Chemical diffusion coefficients were derived for both ferritic and austenitic stainless steels by annealing diffusion couples in the temperature range 800 to 1200° C and measuring the resulting concentration profiles using electron probe microanalysis.

Published chromium volume diffusion data for austenitic and ferritic stainless steels are plotted on the Arrhenius plot, Fig. 1. The most common method for the determination of diffusion coefficients is by observing the penetration of a radioactive isotope into the steel substrate. For stainless steels only two studies have previously measured diffusion coefficients from diffusion couples, that is Ericsson *et al.* [2] and Alberry and Kyte [3].

To understand many metallurgical processes, such as alloy depletion during corrosion, chemical diffusion coefficients and not tracer diffusion coefficients are required. Chemical and tracer diffusion coefficients can be related by mathematical expressions [4]. However, there are advantages in measuring chemical diffusion coefficients directly, such as the much greater mass transfer which occurs across a diffusion couple than in tracer techniques, which may illustrate possible phase changes during the diffusion process. There is good agreement between the diffusion data of ferritic steels (Fig. 1), but the data for austenitic steels fall into a much wider band. This variation in austenitic diffusion data could arise from the different material compositions and microstructures used, thus showing a need to derive data for individual steels.

2. Experimental procedure

Diffusion couples were machined from commercial co-extruded boiler tubes, supplied by the CEGB. These couples consisted of a mild steel on one side and ferritic AISI 446 or austenitic AISI 310 on the other. The composition and grain size of these alloys are listed in Table I. Co-extruded boiler tubes are formed at 1200° C, using high pressure to ensure a good bond. Electron probe micro-analysis was used to measure the extent of element diffusion across the interface during co-extrusion. Diffusion couples were encapsulated in quartz tubes, which were flushed with argon prior to sealing. Diffusion couples were annealed for times of sufficient duration to ensure that diffusion which occurred during co-extrusion was negligible. Some chromium plated AISI 446 couples were also produced. After annealing, specimens were mounted in conductive bakelite, with the plane of the couple interface perpendicular to the mount surface. A minimum of 1.5 mm was polished off the exposed surface to avoid edge effects.

Micro-analysis work was performed with a Philips

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*Present address: ETH-Honggerberg/HPF, CH-8093, Zurich, Switzerland.

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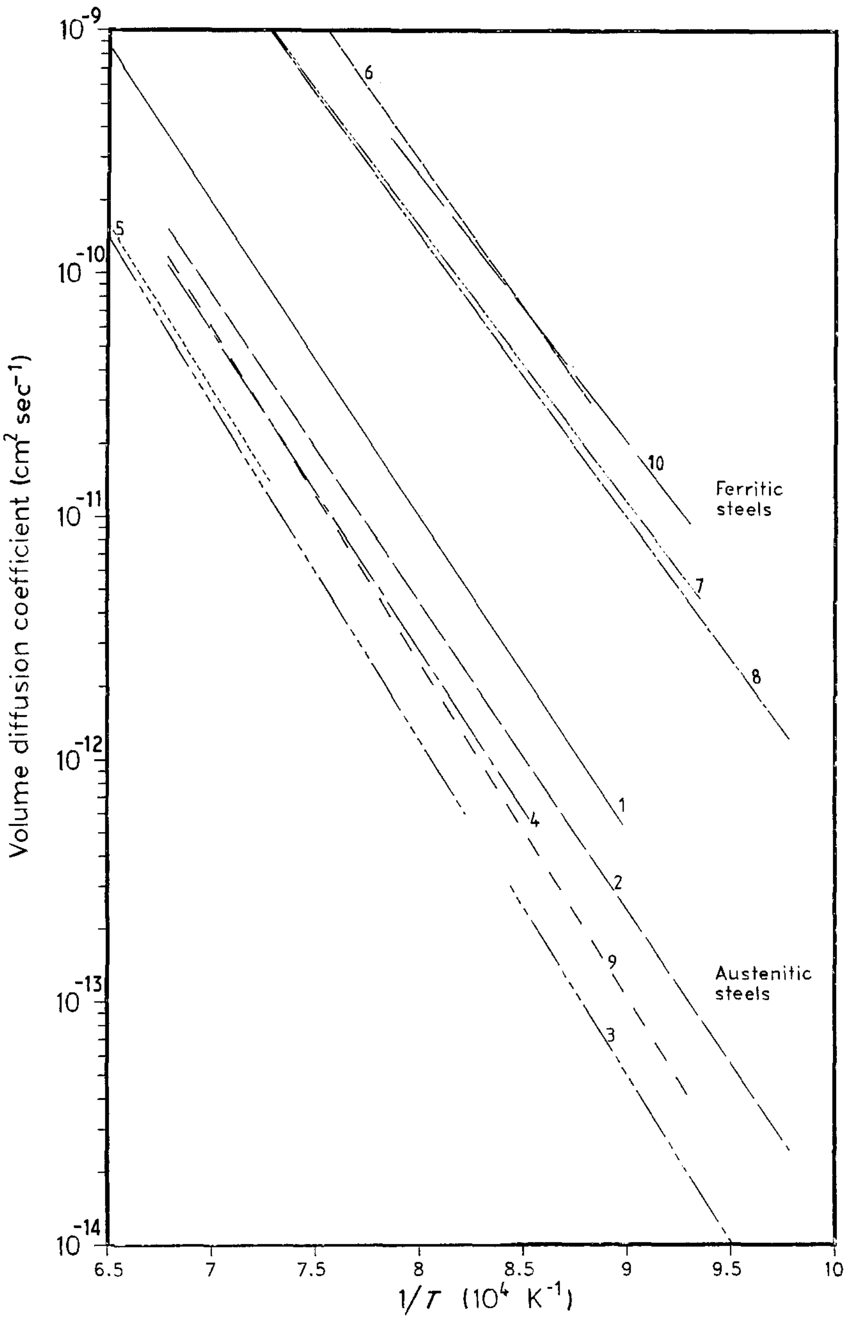

Figure 1 Arrhenius plot of published volume diffusion data. 1, Fe–20Cr–25Ni–Nb [7]; 2, Fe–17Cr–12Ni [8]; 3, Fe–17Cr–12Ni [9]; 4, Fe–16Cr–14Ni–1Si [10]; 5, Fe–0 to 27Cr [14]; 6, Fe–12Cr [17]; 7, Fe–19Cr [15]; 8, Fe–0 to 27Cr [14]; 9, Fe–27Cr–19Ni, present work; 10, Fe–27Cr, present work.

SEM 505 scanning electron microscope using a beam voltage of 25 kV, a beam current of approximately 10 nA, a spot size of less than 100 nm and X-ray take-off angle of 35°. X-rays were counted using the EDAX energy dispersive system, which incorporates software to correct for X-ray absorption, X-ray fluorescence, electron backscattering and X-ray production efficiency. The concentrations of identified elements were normalized to 100%, after these corrections were made. The overall concentration profile of diffusion couples was determined by counting X-rays whilst the electron beam rastered along straight lines parallel to the interface. This averaged out any inhomogeneities in the alloy, such as precipitates, and

TABLE I Material composition, grain size and hardness

Steel	Composition (wt %) balance Fe												Grain size (μm)	Reichaert Micro-hardness (kg mm^{-2})
	Cr	Ni	Mo	Nb	Mn	Si	Cu	Ti	V	P	S	C		
9 Cr/1 Mo	9.2	0.18	0.97	< 0.1	0.59	0.60	0.10	< 0.1	< 0.1	0.013	< 0.01	0.11	21	233 ± 18
AISI 446	25.5	< 0.2	< 0.1	< 0.1	0.62	0.37	< 0.1	< 0.1	< 0.1	0.02	0.012	0.10	32	240 ± 34
AISI 310	~ 27	~ 20	0.24	< 0.1	~ 2	< 1.5	0.08	< 0.1	0.1	0.02	< 0.02	0.05	24	212 ± 32
Aged AISI 310	~ 25	19.4	0.09	< 0.1	~ 2.5	< 1.5	0.05	< 0.1	< 0.1	0.014	0.02	0.08	70 to 140	248 ± 24
AISI 310 + Nb	~ 26	~ 21	0.38	0.62	1.6	< 1.5	0.05	< 0.1	< 0.1	0.015	< 0.02	0.05	27	199 ± 11
Mild steel	0.11	0.09	0.02	0	1.05	0.17	0.22	0	< 0.01	0.025	0.028	0.15		

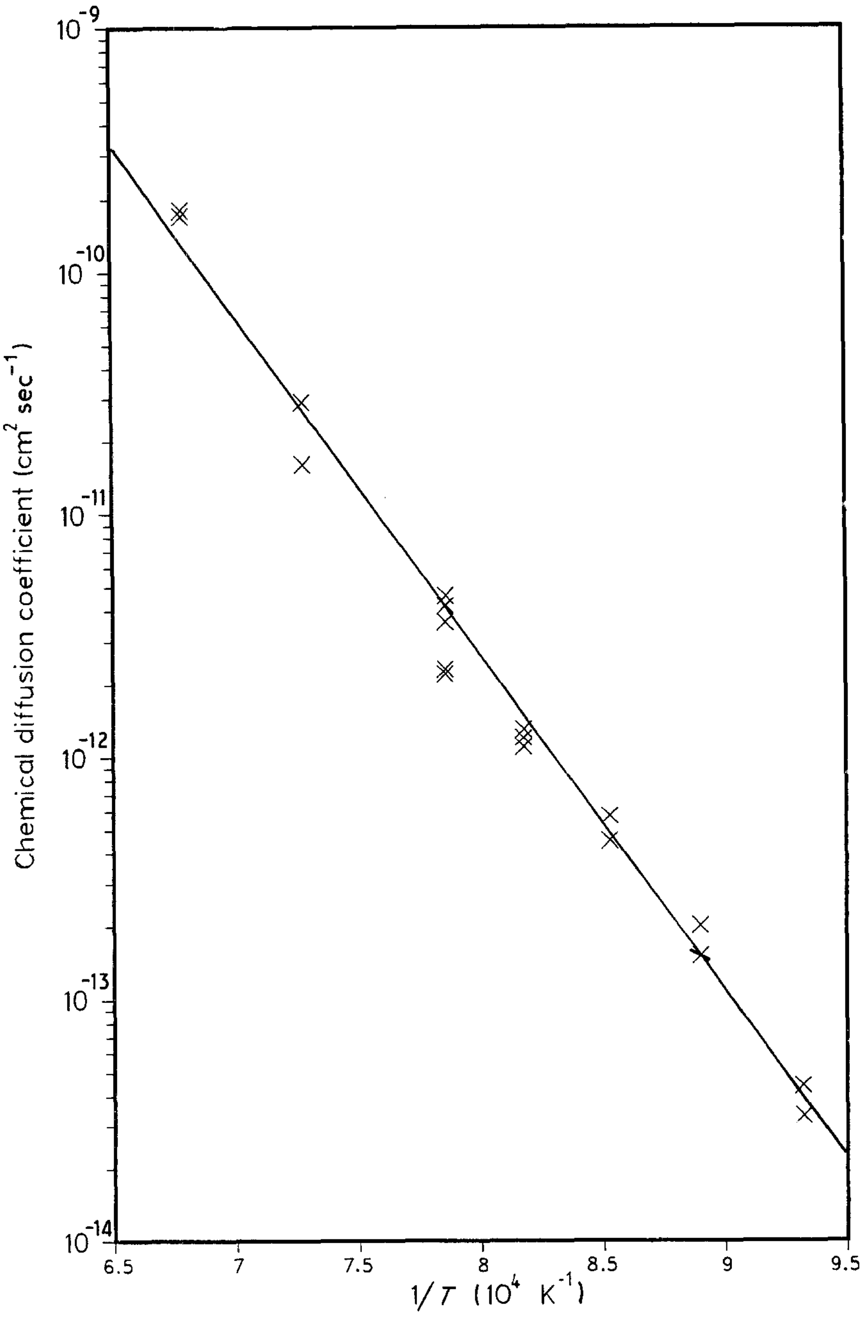

Figure 2 Arrhenius plot of derived diffusion data for AISI 310.

gave an average concentration for a specific distance from the interface. For each couple several analyses, along lines parallel to the interface were taken, the spacing of which depended on the rate of change of element concentration with distance at that location.

3. Discussion and results

The lack of any sudden discontinuities in the concentration profiles of austenitic AISI 310/mild steel couples indicates the phase on both sides is the same. Mild steel is austenitic at the annealing temperatures used because of the presence of carbon and manganese (Table I), which help stabilize the austenitic phase. Thus the Matano–Boltzmann analysis [5], applicable to single-phase systems, can be used to calculate the diffusion coefficients $\tilde{D}(c)$ of the austenitic stainless steels, using the following expression

$$\tilde{D}(c) = \frac{1}{2t}\frac{dx}{dc}\int_c^{c_0} x \, dc$$

where c is concentration, x is distance from the Matano interface, t is the diffusion time, and dx/dc is the reciprocal of the c–x plot at c. Diffusion coefficients can be calculated numerically with the aid of a computer program. An average diffusion coefficient is determined for concentrations greater than 14 at % chromium, to ensure only data from the stainless steel side of the couple are used. Calculated diffusion coefficients for AISI 310 are plotted on the Arrhenius plot, Fig. 2, from which the volume diffusion coefficient for AISI 310, in the temperature range 800 to 1200° C, is found to be:

$$\tilde{D} = 0.27\left(\begin{matrix}+1.04\\-0.22\end{matrix}\right)\exp\left(\frac{-264(\pm 16)}{RT}\right)\mathrm{cm^2\,sec^{-1}}$$

where R is in kJ K^{-1} mol^{-1} and the errors quoted are the 95% confidence limits.

Concentration profiles of ferritic AISI 446/mild steel couples, annealed at 800 to 1000° C, showed discontinuities. This is because the stainless steel side of the couple is ferritic, whereas the mild steel side is austenitic. As chromium diffuses into the austenitic

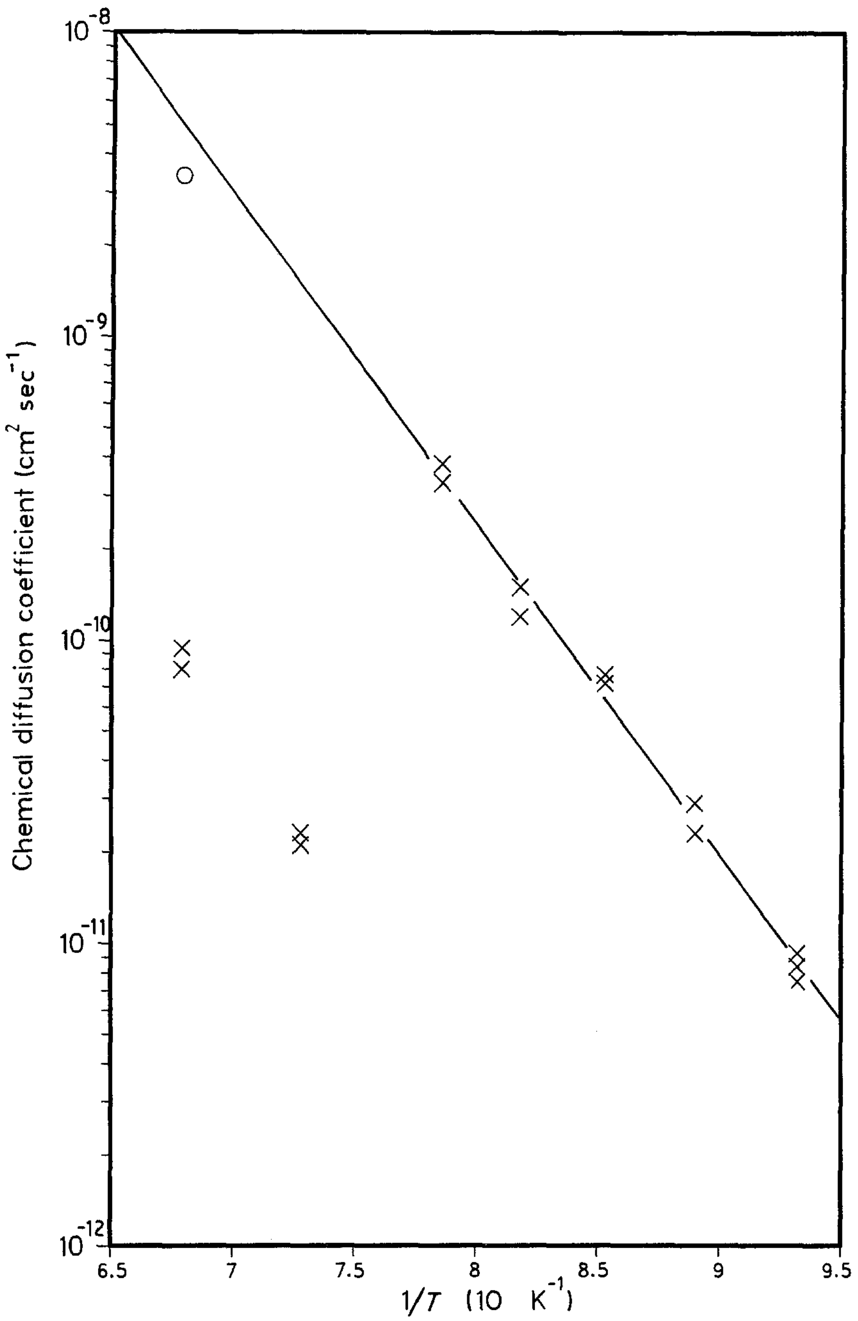

Figure 3 Arrhenius plot of derived diffusion data for AISI 446; (x) co-extruded couple, (o) chromium-plated couple.

mild steel the ferritic phase is stabilized and thus the interface between the two phases moves. An analysis of this diffusion system is given by Jost [6]. For the AISI 446/mild steel couples studied here, the chromium concentration, C, in the ferritic AISI 446 side of the moving interface is given by:

$$C = C_0 - B\left[1 + \mathrm{erf}\left(\frac{x}{2(DT)^{1/2}}\right)\right]$$

where C_0 is the initial chromium concentration in the AISI 446, B is an integration constant, x is the distance from the initial interface and D is the volume diffusion coefficient in AISI 446. From measured concentration profiles the above expression can be used to calculate the diffusion coefficients in AISI 446, for the temperature range 800 to 1000° C. At 1100 and 1200° C the concentration profiles show no discontinuities, implying a single-phase system and that AISI 446 is austenitic at these temperatures. Therefore, for these two temperatures, the Matano–Boltzmann analysis is applied. Derived diffusion coefficients from the AISI 446/mild steel couples are plotted on the Arrhenius graph, Fig. 3, from which the volume chemical diffusion coefficient for AISI 446 in the temperature range 800 to 1000° C is given by:

$$\tilde{D} = 0.15\left(\begin{matrix}+0.54\\-0.12\end{matrix}\right)\exp\left(\frac{-210(\pm 15)}{RT}\right)\ \mathrm{cm^2\,sec^{-1}}$$

The diffusion coefficients at 1100 and 1200° C are nearly two orders of magnitude less than those expected by extrapolation of data obtained at lower temperatures. This is due to AISI 446 being austenitic at the higher temperatures.

The derived data are compared with other published diffusion data in the Arrhenius plot, Fig. 1. This shows good agreement between the diffusion coefficients determined here, for both AISI 446 and AISI 310, and that of previously published data for different material compositions. Ferritic AISI 446 has a diffusion coefficient at least two orders of magnitude larger than austenitic AISI 310, in accordance with previously

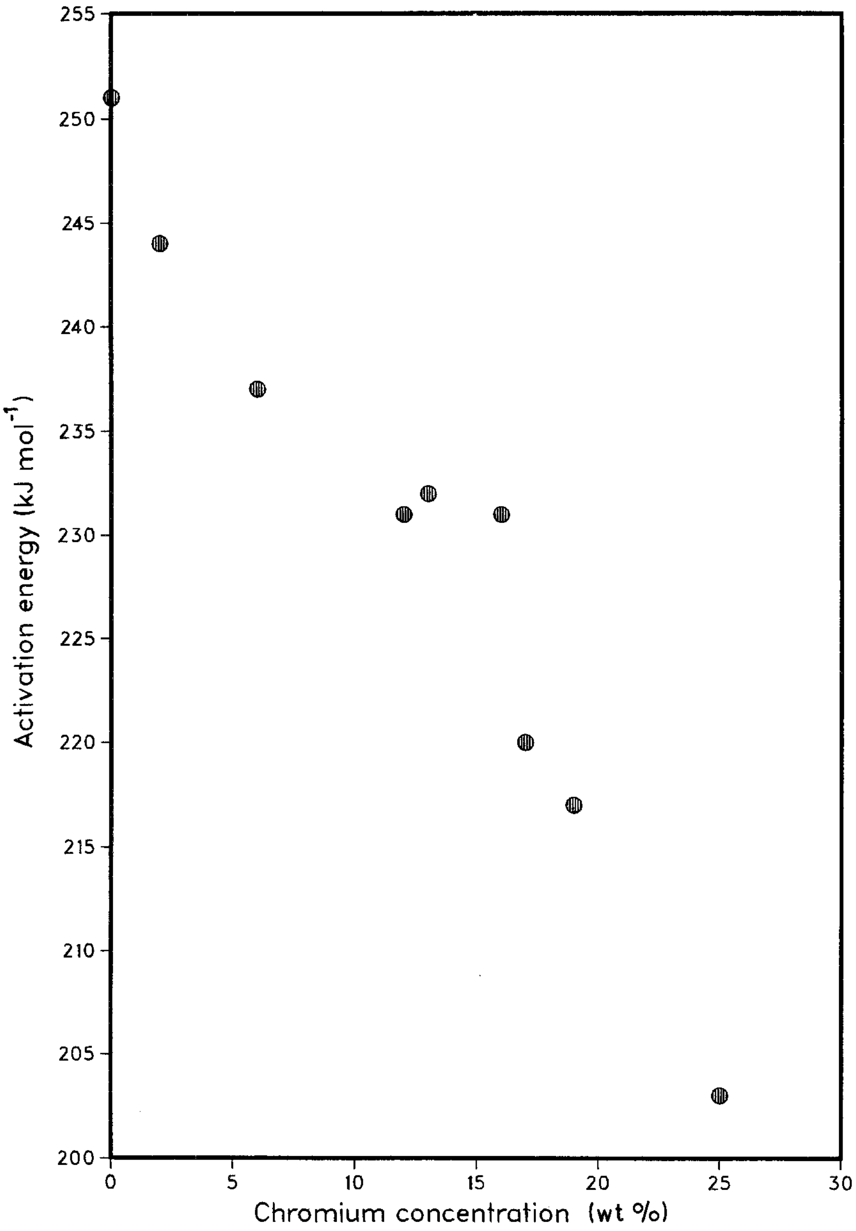

Figure 4 Activation energy for chromium volume diffusion in Fe–Cr alloys.

published data. The activation energy for AISI 310 is 264 kJ mol^{-1}, agreeing with activation energies previously published (Table II). The data for AISI 446 was obtained in the composition range 15 to 28 at % Cr. Published ferritic steel activation energies (Table III) are plotted as a function of chromium concentration in Fig. 4. For the composition range 15 to 28 at % Cr, published activation energies range

TABLE II Chromium volume diffusion data in austenitic steels

Composition	Temperature range (° C)	D_0 (cm^2 sec^{-1})	Q (kJ mol^{-1})	Technique used	Reference	Line on Fig. 1
Fe–20Cr–25Ni–Nb	840–1240	$0.19\left(\begin{array}{c}+0.10\\-0.07\end{array}\right)$	246(±15)	Tracer	[7]	1
Fe–17Cr–12Ni	750–1200	$0.063\left(\begin{array}{c}+0.087\\-0.04\end{array}\right)$	243(±3)	Tracer	[8]	2
Fe–17Cr–12Ni	600–1300	0.13	264	Tracer	[9]	3
Fe–16Cr–14Ni–1Si	900–1200	$0.086\left(\begin{array}{c}+0.045\\-0.03\end{array}\right)$	251(±4)	Tracer	[10]	4
Fe–20Cr–10Ni	943–1038	3.1	283	Tracer	[11]	
Fe–19Cr–10Ni	943–1038	5.6	296	Tracer	[12]	
Fe–15Cr–20Ni	960–1400	$8.3\left(\begin{array}{c}+21\\-3.3\end{array}\right)$	309(±11)	Tracer	[13]	
Fe–15Cr–20Ni–Si	960–1400	$7.1\left(\begin{array}{c}+15\\-3.3\end{array}\right)$	303(±9)	Tracer	[13]	
Fe–O to 27Cr	1100–1350	$0.1\left(\begin{array}{c}+0.1\\-0.05\end{array}\right)$	259(±9)	Diffusion couple	[14]	5
Fe–20Cr–20Ni	800	$D = 1.5 \times 10^{-13}$		Diffusion couple	[2]	
Fe–20Cr–40Ni	800	$D = 3.5 \times 10^{-13}$				
Fe–20Cr–40Ni	1000	$D = 2.3 \times 10^{-11}$				

TABLE III Chromium volume diffusion data in ferritic steels

Composition	Temperature range (° C)	D_0 ($\text{cm}^2\,\text{sec}^{-1}$)	Q ($\text{kJ}\,\text{mol}^{-1}$)	Technique used	Reference	Line on Fig. 1
Fe		$8.52\begin{pmatrix}+3.20\\-2.33\end{pmatrix}$	251(±7)		[15]	
Fe-2Cr	797-1402	$3.21\begin{pmatrix}+0.83\\-0.66\end{pmatrix}$	244(±5)	Tracer	[16]	
Fe-6Cr	797-1402	$1.21\begin{pmatrix}+0.73\\-0.46\end{pmatrix}$	237(±10)	Tracer	[16]	
Fe-12Cr	861-1422	1.29	231	Tracer	[17]	6
Fe-13Cr	797-1402	0.64 (±0.07)	232(±3)	Tracer	[16]	
Fe-16Cr	797-1402	$0.19\begin{pmatrix}+0.03\\-0.02\end{pmatrix}$	231(±4)	Tracer	[16]	
Fe-17Cr	861-1422	0.46	220	Tracer	[17]	
Fe-19Cr	797-1402	$0.18\begin{pmatrix}+0.05\\-0.04\end{pmatrix}$	217(±6)	Tracer	[16]	7
Fe-25Cr	950-1250	0.156	203	Tracer	[18]	
Fe-25Cr-5Ni	600-1000	$0.06\begin{pmatrix}+0.11\\-0.03\end{pmatrix}$	212(±5)	Tracer	[19]	
Fe-O to 27Cr	750-1400	$2.2\begin{pmatrix}+5.0\\-4.0\end{pmatrix}$	240(±2)	Diffusion couple	[14]	8

from 203 to 231 $\text{kJ}\,\text{mol}^{-1}$. Thus the activation energy of 210 $\text{kJ}\,\text{mol}^{-1}$ for AISI 446 agrees with those previously published for ferritic steels. The agreement in activation energies with those previously published, for both ferritic and austenitic steels shows that volume diffusion is being observed.

During the anneal of a diffusion couple, much larger quantities of matter are transferred compared to tracer techniques. In the former technique diffusion is being studied at chromium concentrations lower than the bulk alloy composition, compared to the latter where the chromium concentration is slightly above or equal to the bulk alloy composition. The general direction of chromium movement in a couple is outwards from the stainless steel, as opposed to inwards for tracer techniques. The former results in the dissolving of any chromium-rich phases and this was observed in the present study. The analysis of alloy depletion during corrosion requires the average chemical diffusion coefficient for the composition range of the chromium-depleted zone, which can be derived directly from diffusion couples. Therefore it can be said that of the two experimental techniques, diffusion processes in a couple more closely resemble the actual diffusion mechanisms which occur during alloy depletion in corrosion.

4. Conclusions

The average chemical volume diffusion coefficent, for the composition range 14 to 28 at % chromium, for ferritic AISI 446 in the temperature range 800 to 1000° C is:

$$\tilde{D} = 0.15\begin{pmatrix}+0.54\\-0.12\end{pmatrix}\exp\left(\frac{-210(\pm 15)}{RT}\right)\text{cm}^2\,\text{sec}^{-1}$$

and for austenitic AISI 310 in the temperature range 800 to 1200° C is:

$$\tilde{D} = 0.27\begin{pmatrix}+1.04\\-0.22\end{pmatrix}\exp\left(\frac{-264(\pm 16)}{RT}\right)\text{cm}^2\,\text{sec}^{-1}$$

where R is in $\text{kJ}\,\text{K}^{-1}\,\text{mol}^{-1}$.

Diffusion processes in a diffusion couple are similar to those which occur in the alloy during corrosion, if chromium depletion of the surface region is observed.

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References

1. P. I. WILLIAMS, R. G. FAULKNER, L. W. PINDER and D. J. LEES, *Corros. Sci.* (1986).
2. T. ERICSSON, L. G. LILJESTRAND, S. SCHLSTEDT and H. STERNER, *JISI* **208** (1970) 1109.
3. P. J. ALBERRY and W. S. KYTE, *Met. Sci.* **12** (1978) 515.
4. L. S. DARKEN, *Trans AIME* **175** (1948) 184.
5. P. J. SHEWMAN, "Diffusion in Solids" (McGraw-Hill, New York, 1963) p. 30.
6. W. JOST, "Diffusion", 2nd Edn (Academic, London, 1960).
7. A. F. SMITH and G. B. GIBBS, *Met. Sci.* **3** (1969) 93.
8. A. F. SMITH, *ibid.* **9** (1975) 375.
9. R. A. PERKINS, J. R. PADGETT and N. K. TUNALI, *Metall Trans.* **4** (1973) 2535.
10. W. ASSASSA and P. GUIRALDENQ, *Met. Sci.* **12** (1978) 123.
11. H. S. DARUVALA and K. R. BUBE, *Mat. Sci. Eng.* **41** (1979) 293.
12. *Idem, J. Nucl. Mater.* **87** (1979) 211.
13. S. J. ROTHMAN, L. J. NOWICKI and G. E. MURCH, *J. Phys. F Met. Phys.* **10** (1980) 383.
14. P. J. ALBERRY and C. W. HAWORTH, *Met. Sci.* **8** (1974) 407.
15. A. W. BOWEN and G. M. LEAK, *Met. Trans.* **1** (1970) 1695.
16. *Idem, ibid.* **1** (1970) 2767.
17. R. A. WOLFE and H. W. PAXTON, *Trans TMS-AIME* **230** (1964) 1426.
18. H. W. PAXTON and T. KUNITAKE, *ibid.* **218** (1960) 1003.
19. A. F. SMITH and R. HALES, *Met. Sci.* **10** (1976) 418.

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