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Effect of alloying elements on hydrogen diffusivity in α-iron

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The effect of Cr, Ni, Mo, Si and Cu on the diffusivity of hydrogen in α-iron is studied in the temperature range of 160 to 430° C at a hydrogen pressure of 1 atm. The diffusivity of hydrogen was determined by absorption rate experiments using Sievert's type apparatus. The results show that the diffusivity of hydrogen in iron alloys decreases and the activation energy increases, as the concentration of the alloying elements increases, except Cu and Ni. The trapping parameters of hydrogen in iron alloys on the basis of Oriani's approach are calculated. The results show that Si, Mo and Cr are in order of increasing trap energy and that Cu and Ni have a negligible effect on hydrogen trapping. This can be explained by taking account of both chemical affinity effects and elastic strain effects of alloying elements on hydrogen trapping.

1. Introduction

The effect of hydrogen on the mechanical properties of iron was studied by Pfeil [1] and his results showed that ductility of iron is decreased markedly when hydrogen is occluded in it. Since his study, a number of investigators have reported the anomalous behaviour of hydrogen in iron and steels.

It has been found that the diffusivity of hydrogen in iron and steels deviates markedly, at low temperature, from that predicted by the extrapolation of higher temperature data to lower temperature. The overall variation of the diffusivity of hydrogen as a function of temperature has been plotted in Fig. 1 from a representative selection of published results.

In the lower temperature region, two points are to be noted, the first being that the measured apparent diffusivity is generally at least one or two orders of magnitude smaller than the lattice diffusivity, while the second is that the apparent activation energy in this region is generally in the range 8 to 44 KJ mole^{-1}.

This kinetical abnormality leads to the supposition that hydrogen is being retained in some form of energy favoured trap in the low temperature region. The nature and mechanism of trapping have been the subject of much speculation and discussion. The nature of identified traps in iron includes the variable defects such as grain boundaries, dislocations, voids and internal interfaces [2, 3]. According to some investigators [2, 3], some alloying elements such as Ti in iron may play an important role in hydrogen trapping through its chemical and electronic influence on the interaction of iron matrix and hydrogen (Fig. 2).

While it is in general difficult to distinguish one kind of trap from another due to their complex interaction, certain trap characteristics of one specific kind may be analysed if one can control it independently of the other traps. The purpose of the present work is to study the influence of alloying elements Ni, Cr, Mo, Si and Cu on the diffusivity and activation energy of hydrogen in α-iron and to estimate, from these kinetic data, trap energy of the alloying elements following Oriani's model, with a view to contributing to the comprehension of their hydrogen trapping effect.

2. Materials and experimental method

The base material for this study consited of electrolytic iron to which specific quantities of alloy-

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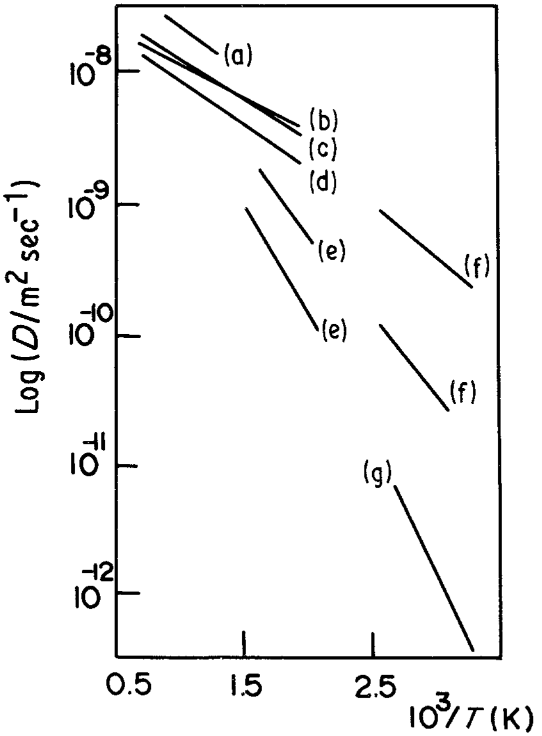

Figure 1 Published data for the diffusivity of hydrogen in iron and steels. (a) Geller and Sun [14], (b) Sykes *et al.* [7], (c) Eichenhauer *et al.* [15], (d) Stross and Tompkins [23], (e) Hill and Johnson [20], (f) Frank *et al.* [21], (g) Barrer [22].

ing element Ni, Cr, Mo, Si and Cu were added in the α range. The alloys studied were vacuum melted (2×10^{-2} mm Hg) in an induction furnace and homogenized for 48 h in the temperature range 1000 to 1100° C to fully disperse the alloying elements added. Cylindrical specimens of various sizes were machined from the prepared ingots as above. Before thermal hydrogenation, all test specimens of cylindrical shape were subjected to a pretreatment consisting of degassing for 2 h under a high vacuum (1×10^{-5} mm Hg) at 700° C, to avoid surface impedance. High purity (5N) hydrogen gas was used.

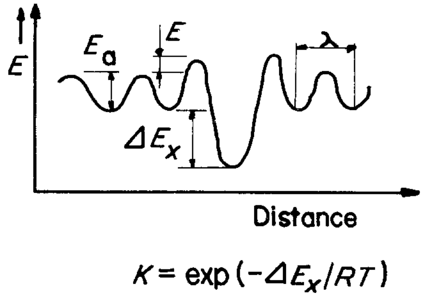

Figure 2 Model for trapping site [3].

For comparative purposes, experiments were conducted using pure iron supplied by ESPI. The purity of electrolytic iron and the pure iron is given in Table I and the composition of the alloying elements in iron alloys studied is given in Table II.

Diffusivity of hydrogen in iron and iron alloys was studied in the temperature range of 160 to 430° C at a hydrogen pressure of 1 atm by the measurement of hydrogen absorption rate in Sievert's type apparatus [5]. Hydrogen gas was introduced and maintained at a constant pressure of 1 atm in the reaction tube. As the hydrogen gas diffused into the specimen placed in the reaction tube, the volume of hydrogen gas in the reaction tube was reduced by the amount equivalent to the volume of hydrogen gas absorbed by the specimen. The magnitude of this change is measured as a function of time and converted into STP volume.

3. Results and discussion

It is necessary to consider classical diffusion in a cylindrical medium in order to obtain the diffusivity of hydrogen from the absorption curves measured in iron and its alloys. Crank [6] derived a convenient solution of the appropriate equation for Fick's second law. The equation takes, for cylindrical shape, the form

$$\ln\left(1-\frac{\Delta V(t)}{\Delta V(\infty)}\right) = \ln\frac{32}{\pi^2 B_1^2} - \frac{D}{r^2} \times \left[\left(\frac{r\pi}{l}\right)^2 + B_1^2\right] t \quad (1)$$

where $\Delta V(t)$ is absorbed STP volume at time t, $\Delta V(\infty)$ is total absorbed STP volume, r is radius of the specimen, l is length of the specimen and B_1 is 2.405.

The measured absorption rate $\ln 1 - [\Delta V(t)/\Delta V(\infty)]$ against time was plotted for various temperatures as a representative curve for Fe–1.5 wt% Ni alloy which is shown in Fig. 3. Straight lines resulted and the diffusivity of hydrogen in iron

TABLE I Chemical composition of electrolytic and pure iron (ppm by weight)

	Fe	Ni	Cr	Si	O	C	Mn
Pure iron	5N*	Z	–	1	–	–	3
Electrolytic iron	3N5*	–	–	–	–	50	–

*(5N = 99.999 wt%, 3N5 = 99.95 wt%).

TABLE II Weight per cent of the alloying elements in the iron alloys

Alloying element	Weight per cent	Alloying element	Weight per cent	Alloying element	Weight per cent
Ni	1.50 2.20 3.21	Cr	0.90 2.30 3.05	Si	0.72 1.38 1.96 1.96
Mo	0.77 1.80 3.30	Cu	0.19 0.31 0.51		

and its alloys was calculated at each temperature from the slopes of these lines. The results of Fig. 3 show very good lineality (with 95% confidence), and indicate that the diffusion process controls the behaviour of hydrogen in the specimens of iron and its alloys tested. It is believed that it proves the negligibility of surface impedance in the tested specimens. For that purpose, we have selected two different sizes of the same specimen with $d = 1.56$ cm, $l = 2.68$ cm and $d = 0.50$ cm, $l = 6.60$ cm. Here d and l designate the diameter and length of the cylindrical specimens. The measurement of diffusivity of hydrogen on the two different sized specimens shows the same results within experimental error. It is believed that this confirms that surface impedance of the tested specimens is practically negligible under our experimental conditions. The activation energies of hydrogen in each alloy, E_D, are calculated from the diffusivities of hydrogen in each alloy, D, using Arrhenius equation

$$D = D_0 \exp(-E_D/RT) \tag{2}$$

where D_0 is the diffusion coefficient, R is the gas constant and T is absolute temperature.

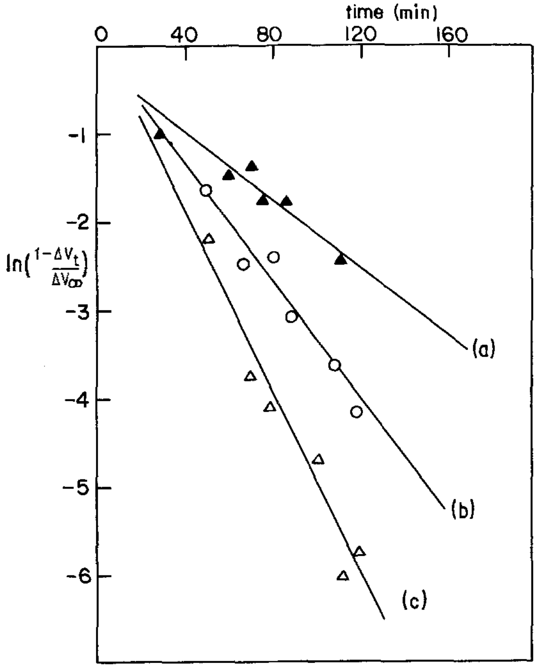

Figure 3 Volume change as a function of time in Fe–1.5 wt% Ni at various temperatures. (a) 170° C, (b) 208° C, (c) 322° C.

The results for D_0 and E_D in pure iron and α-iron are presented in Table III and the values obtained by a number of investigators are also given for comparison purposes, with the relevant experimental information. One can realize easily from this table that these data are quite different, depending on the experimental technique used and the purity of the specimen studied. However, the value of activation energy E_D in electrolytic iron is nearly identical to that in pure iron in the case of our results and these values correspond fairly well to those given by Sykes [7] and Subramanyan [8] in spite of the different experimental techniques employed.

The values of activation energy for each alloy are shown in Figs 4 to 8 as a function of concentration of alloying elements. The general trend is that the activation energies of hydrogen increase with an increase in the amount of alloying elements of Cr, Mo and Si, while Cu and Ni have a negligible effect on the activation energy. It is believed that these results indicate that hydrogen can be trapped by certain alloying elements.

Oriani [3] has shown that when a local equilibrium between trapped and diffusing populations is assumed, the apparent diffusivity becomes

$$D_{\text{app}} = D_L \frac{C_L}{C_L + C_T(1-n)} \tag{3}$$

where D_L is the lattice diffusivity of hydrogen, C_L is the lattice concentration of hydrogen, C_T is the trapped concentration of hydrogen and n is the fractional occupancy of traps. He has also

TABLE III Summary of the diffusivities of hydrogen in iron

Reference	Experimental method	Material	Temperature range (°C)	D_0 (× 10^8 m^2 sec^{-1})	E_D (J mole^{-1})
This work	Absorption rate	Pure iron	270–430	8.05	9483
This work	Absorption rate	Electrolytic iron	160–340	23.80	9818
[7]	Permeability	α-Fe	0–900	7.60	9546
[14]	Permeability	α-Fe	400–900	22.00	12142
[15]	Evolution rate	Armco iron	200–774	9.30	11305
[16]	Permeability	Armco iron	10–75	6.00	5447
[17]	Permeability	Pure iron	300–900	6.40	8039
[8]	Permeability	Pure iron	10–70	2.50	9211

shown that in the region of low coverage of hydrogen in the trap, $n \simeq 0$, Equation 3 is independent of the concentration of hydrogen and becomes

$$D_{\text{app}} = D_L(1 + KN_x/N_L)^{-1} \qquad (4)$$

where K is the equilibrium constant and $K = \exp(-\Delta E_x/RT)$ (here ΔE_x is trap energy as shown in Fig. 2), N_x is the density of the trapping sites and N_L is the density of the lattice sites. Equation 4 can be rearranged into Equation 4a

$$\frac{D_L}{D_{\text{app}}} = 1 + \frac{K}{N_L}\,N_x. \qquad (4a)$$

The significance of Equation 4a is that if one can control the trap density, N_x of one specific reversible trap x and measure the resulting variation of apparent diffusivity, D_{app}, one can calculate trap energy, E_x, of that trap from the value of equilibrium constant $K = \exp(-\Delta E_x/RT)$.

Now assuming that the alloying elements constitute major trap sites compared to the other trap natures, one may apply Equation 4a to the present results of the apparent diffusivity variation with the content of alloying elements in α-iron matrix. In Equation 4a, we take for D_L the experimental diffusivity value for electrolytic iron assuming that the trap density of the other traps is insignificant compared to the alloying elements. Trap sites may be any of the six octahedral sites ($Z = 1$ to 6) nearest to the alloying element if it is valid that the substitutional alloying elements constitute major trap sites. According to Pressouyre and Bernstein [2], the value of Z is close to 1 in the case of Ti in α-iron. Remembering that the present purpose is to calculate trap energies between various alloying elements and hydrogen rather than to calculate K, we take N_x as the atomic density of alloying element (i.e. $Z \simeq 1$). N_L is the number of the octahedral sites

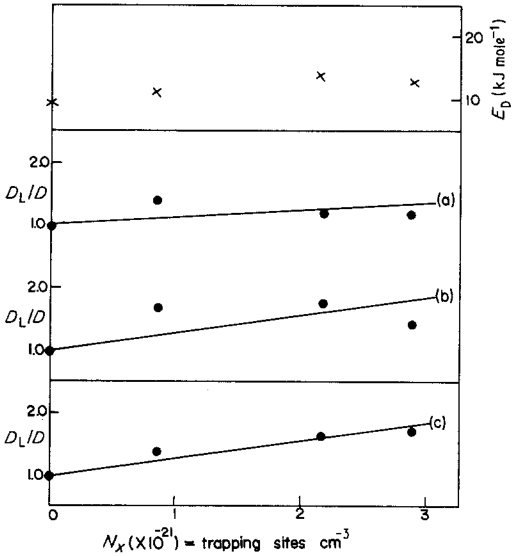

Figure 4 Effect of Cr on D_L/D and activation energy of hydrogen in Fe–Cr alloys at various temperatures. (a) 322° C, (b) 208° C, (c) 170° C.

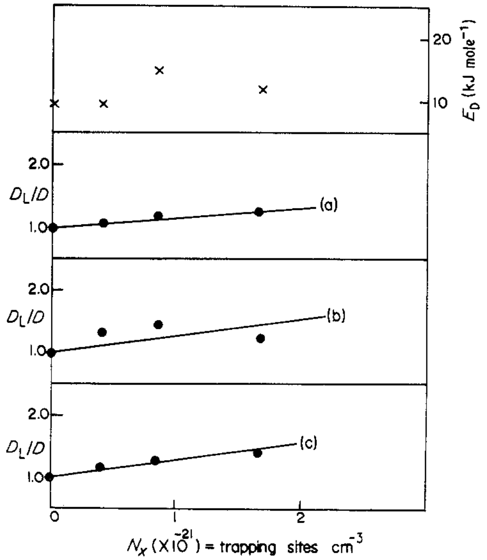

Figure 5 Effect of Mo on D_L/D and activation energy of hydrogen in Fe–Mo alloys at various temperatures. (a) 322° C, (b) 253° C, (c) 170° C.

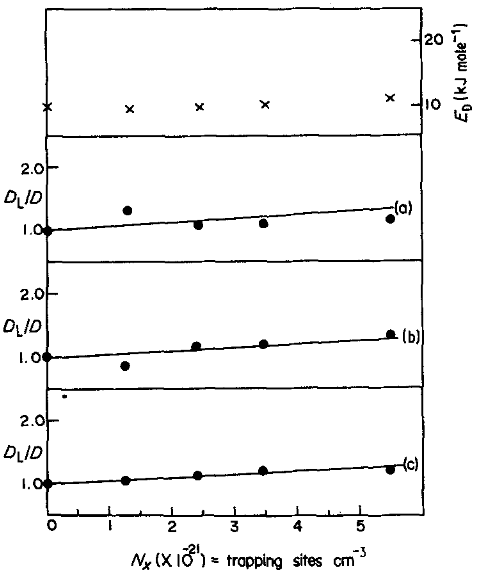

Figure 6 Effect of Si on D_L/D and activation energy of hydrogen in Fe–Si alloys at various temperatures. (a) 322° C, (b) 208° C, (c) 170° C.

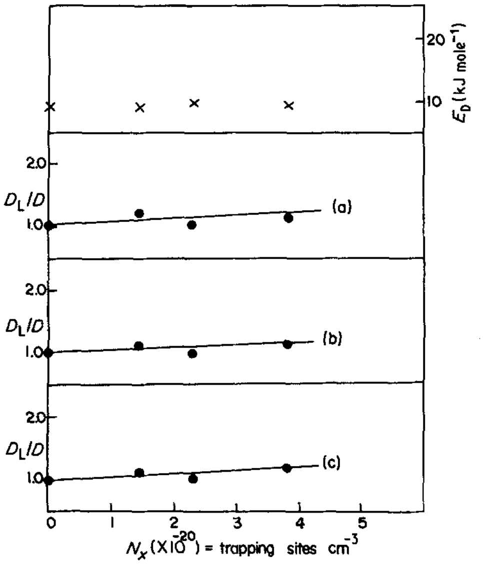

Figure 8 Effect of Cu on D_L/D and activation energy of hydrogen in Fe–Cu alloys at various temperatures. (a) 322° C, (b) 253° C, (c) 208° C.

in bcc iron and the calculated value of N_L is 2.6×10^{23} sites cm^{-3}.

Figs 4 to 8 show the variation of apparent diffusivity D_L/D_{app} with the density of each alloying element Cr, Mo, Si, Ni and Cu at various temperatures, respectively. These figures generally show a linear behaviour. This supports the assumption that the above alloying elements constitute reversible traps at low concentrations. From the slopes of these lines, the values of the equilibrium constant, K, for each temperature are calculated. The values of trap energy, ΔE_x of each alloying element are obtained from the temperature dependence of the equilibrium constant. These results are given in Table IV.

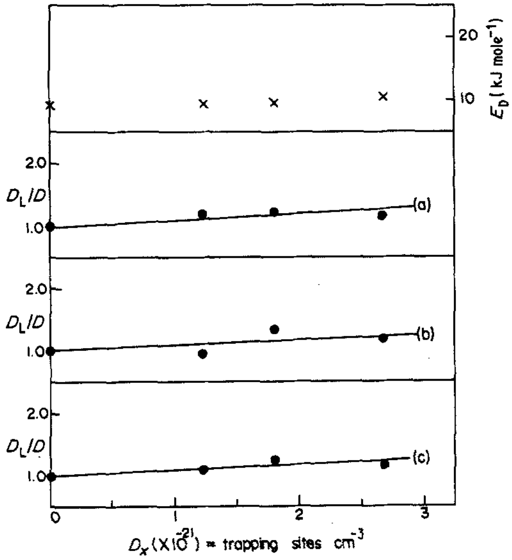

Figure 7 Effect of Ni on D_L/D and activation energy of hydrogen in Fe–Ni alloys at various temperatures. (a) 322° C, (b) 208° C, (c) 170° C.

In applying Equation 4a to our results, it is assumed that the traps are sparingly occupied. At equilibrium, it can be shown that the fractional occupancy of traps, n_e becomes [9]

$$n_e = \frac{KC_L/N_L}{1 + KC_L/N_L}. \tag{5}$$

Hydrogen solubility at 322° C gave a value for C_L of 10^{18} atoms H_2 cm^{-3}. Using the values of K in Table IV, n_e is always lower than $\sim 10^{-3}$. This proves that the traps in these cases are sparingly occupied.

It is true to say that the present results are not extensive enough to analyse the magnitude of the equilibrium constant and the trap energy for each alloying element exactly and that an analysis made in this way is necessarily approximate because of the many assumptions included. However, a special estimation may be made from the results in Table IV. In Table IV, one finds that the absolute values of trap energy $|\Delta E_x|$ of Si, Mo and Cr are in order of increasing magnitude, while that of Ni and Cu is nearly equal to zero. These results may be explained by taking account of both chemical affinity effects and elastic strain

TABLE IV Trapping parameters of iron alloys

Alloying element	Trap density ($\times 10^{-20}$ sites per cm^3)	Temperature (°C)	K	Trap energy ($-\Delta E_X$) (KJ mole^{-1})
Cr	8.31	170	68.53	17.4
	21.45	208	60.39	
	28.75	322	21.79	
Mo	3.81	170	72.93	11.0
	8.56	253	50.41	
	16.45	322	33.48	
Si	12.30	170	12.86	1.8
	23.91	208	14.66	
	34.43	322	11.79	
	55.29			
Ni	12.04	170	23.38	~ 0
	18.06	208	25.32	
	26.63	322	23.87	
Cu	1.44	208	139.08	~ 0
	2.29	253	137.04	
	3.82	322	141.56	

effects of each alloying element on hydrogen trapping.

If an alloying element has a higher "affinity" for hydrogen than the host atoms, there will be a thermodynamic attraction which is roughly proportional to the first order interaction coefficient, e_i^H [10, 11]. Here i designates alloying element dissolved in iron. A negative value of e_i^H indicates a thermodynamic attraction between i and H and a positive value of e_i^H means a thermodynamic repulsion between i and H. The more negative e_i^H, the stronger the attraction, and vice versa.

Furthermore the interaction between interstitial and substitutional atoms could result in an attraction or repulsion depending on whether the substitutional atom is smaller or larger than the host atoms, because of their strain field interactions [12]; that is, if the value of the strain field, $\epsilon = (\gamma_m - \gamma_{Fe})/\gamma_{Fe}$ is negative, the interaction between substitutional atom M and hydrogen is attractive and when the value of ϵ is positive, it is repulsive. The more negative ϵ, the stronger the attraction. Here γ designates radius of the metal atom.

Table V shows the results of trap energy for each alloying element Cr, Mo, Si, Ni and Cu. This table also shows the reference data of the interaction coefficient, e_i^H, and the size mismatch term, ϵ, for each alloying element. The tabulated reference values of e_i^H are those for elements at liquid iron temperature. It has been shown [13] that the same relative rankings are obeyed when corrected to room temperature. It can be estimated from this table that Si, due to its large negative size mismatch, exhibits a small trapping effect in spite of the large positive value of e_{Si}^H and that in the case of Mo, its size difference appears to play an important role. Such considerations of both chemical effects and strain effects on hydrogen trapping leads to the explanation of the fact observed that Si, Mo and Cr are in the order of increasing trap energy. On the other hand, it is thought that Ni and Cu have a negligible effect on hydrogen trapping because of their small chemical affinity and size mismatch.

TABLE V Parameters affecting alloying element hydrogen interactions in iron

Alloying element	Trap energy (KJ mole^{-1})	Reference [18] (e_i^H)	Reference [19] (e_i^H)	Size mismatch, ϵ (%)
Cr	17.4	− 0.11	− 0.11	+ 0.65
Mo	11.0	–	− 0.12	+ 9.59
Si	1.8	+ 0.76	–	− 5.24
Ni	0	0	− (0.00)	+ 0.32
Cu	0	+ 0.03	–	+ 2.98

4. Conclusions

The results of absorption rate studies of hydrogen in iron and its alloys show that the diffusion of hydrogen in iron alloys of particularly Cr, Mo and Si is slower than in pure iron and electrolytic iron and becomes even slower as the concentration of the alloying elements increases. This is interpreted as being due to trapping of hydrogen atoms by alloying elements.

The values of hydrogen trap energy for each alloying element Si, Mo, Cr, Cu and Ni obtained from these kinetic data show that Si, Mo and Cr are in order of increasing trap energy, $|\Delta E_x|$, and that Cu and Ni have a negligible trap effect on hydrogen.

This effect of the various alloying elements on the trap energy can be interpreted by taking account of both chemical affinity effects and elastic strain effects of each alloying element on hydrogen trapping.

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