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Stability of hydrogen and nitrogen in group VIa metals (Cr, Mo, W) and iron-group metals (Fe, Co, Ni) evaluated by statistical thermodynamics

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Solubility data of hydrogen and nitrogen in group VIa metals (Cr, Mo, W) and iron-group metals (Fe, Co, Ni) were analysed on the basis of statistical thermodynamics. The stabilities of hydrogen in iron-group metals were estimated to be comparable to one another and the same appeared to be true for nitrogen solutions. On the other hand, stabilities of nitrogen in group VIa metals worsened appreciably as the number of the period increased. The same trend seemed to be valid for hydrogen solution in group VIa metals but with a smaller extent of worsening stability.

1. Introduction

Nitrogen and carbon are representative interstitial alloying constituents to steel materials, and hydrogen absorbed in a steel matrix is known to cause several undesirable consequences, such as hydrogen embrittlement. In order to characterize the behaviour of these interstitial constituents in steel materials, it seems to be essential to evaluate the intensity of the interaction between these interstitial atoms and the metallic constituent elements of steel materials.

Iron-group metals (Fe, Co, Ni) and group VIa metals (Cr, Mo, W) are fundamental metallic components in steels. Thus, it might be of pragmatic significance to evaluate quantitatively the stability of hydrogen and nitrogen in group VIa and iron-group metals. For this purpose, a statistical thermodynamic approach appears to be more suitable than the traditional thermodynamic one, in the sense that absolute levels of stability of different interstitial atoms in a given metal lattice might be derived with a common reference state of energy zero taken at each component atom at rest being in infinite separation in vacuum by statistical thermodynamics [1]. Comparison of this nature is not feasible by traditional thermodynamics because the reference states of interstitial elements are not usually identical. In addition, atomic arrangement models might be developed by carefully analysing interaction parameters derived by statistical thermodynamics [2–8]. Visualizing a model for atomic clustering is not very easy from the traditional thermodynamic approach, but it is not impossible.

In the present work, equilibrium pressure–temperature–composition (*P–T–C*) relationships previously compiled for hydrogen and nitrogen solution in group VIa and iron-group metals [9], will be analysed on the basis of statistical thermodynamics. The aim of this work was to widen the range of available parameters for analysing phase relations of pragmatically important steel systems on the basis of statistical thermodynamics.

2. Hydrogen and nitrogen solubilities in group VIa and iron-group metals

In this work, *P–T–C* relationships for the concerned materials, compiled previously [9], were analysed. In [9], all *P–T–C* data of concern here were filed in a normalised form

$$\log c = (1/2)\log p(\mathrm{X_2}) - A - B/T \qquad (1)$$

where c is the atomic per cent of X in MX_x, $p(\mathrm{X_2})$ the equilibrium pressure of $\mathrm{X_2}$ gas (torr) and T the absolute temperature. *P–T–C* relations for group VIa metals were compiled by Jehn ([9] pp. 521–63, Table I) and those for iron-group metals by Krüger *et al.* and Schürmann ([9] pp. 578–635, Table II).

3. Statistical thermodynamic analysis

The fundamental formulae used for present analysis are [1–8]

$$\begin{aligned} A &\equiv RT\ln\{[(\theta - x)/x]\,[p(\mathrm{X_2})]^{1/2}\} \\ &= K - \mu_{\mathrm{N}}^{0} + \beta x E_{\mathrm{X-X}} \qquad (2) \\ K &= Q - RT\ln f_{\mathrm{X}} \qquad (3) \\ \partial E/\partial n_{\mathrm{X}} &= Q + \beta x E_{\mathrm{X-X}} \qquad (4) \\ \mu_{\mathrm{X}}^{0} &= -(1/2)D(\mathrm{X_2}) + RTC(T) \qquad (5) \end{aligned}$$

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TABLE I Values of factors, A and B, for hydrogen and nitrogen solubility data in group VIa metals given by form of Equation 1 in [9]

MX_x							
M	State	X					
		H			N		
		A	B	T (°C)	A	B	T (°C)
Cr	Solid	0.93 2.53	3000 1330	730–1130 500–730	− 0.1	1410	800–1400
Mo	Solid	1.81	2730	900–1500	0.523	4940	1600–2400
W	Solid	2.40 3.62 1.49	4380 1090 5250	2430–3000 1600–2430 900–1750	0.036	10200	2400–3050

TABLE II Values of factors, A and B, for hydrogen and nitrogen solubility data in iron-group metals given by the form of Equation 1 in [9]

MX_x							
M	State	X					
		H			N		
		A	B	T (°C)	A	B	T (°C)
Fe	Liquid	1.425	1660	1536–1700	2.06	251	1536–1750
	Solid bcc (δ)	1.86	1504	1391–1536	2.02	1330	1400–1536
	fcc (γ)	1.83	1562	910–1391	2.77	− 420	910–1400
	bcc (α)	2.25	1268	200–910	1.60	1825	500–910
Co	Liquid	1.21	2140	1492–1700	2.0	2190	1550–1700
	Solid (fcc)	1.83	1680	1000–1492	Negligible solubility		
Ni	Liquid	1.42	1176	1500–1700	2.45	2340	1550–1700
	Solid (fcc)	2.00	870	350–1400	Negligible solubility		

$$C(T) = -(1/2)\ln\{[(4\pi m_X)^{3/2}(kT)^{5/2}/h^3] \times (T/\Theta_r)(1+\Theta_r/3T)(\rho^2/2)\} + \Theta_v/4T + (1/2)\ln[1-\exp(-\Theta_v/T)] \qquad (6)$$

where R is the universal gas constant, θ a number of available interstitial sites for occupation by X atoms per metal atom in MX_x, μ_X^0 the standard chemical potential of X_2 (1/2 mole, $p(X_2) = 1$ atm) with the reference state being taken as monoatomic X at rest in vacuum, β a factor determined by crystal structure consideration, E_{ij} the interaction energy between component atoms, i and j, in MX_x, Q the extent of stabilization of the X atom in MX_x with reference to an isolated X atom, f_X the atomic partition function of X in MX_x, E the lattice energy of MX_x, n_X number of X atoms in MX_x, $D(X_2)$ the dissociation energy per mole of X_2 molecule, m_X the mass of X atom, k the Boltzmann constant, h the Planck constant, Θ_r the characteristic temperature of rotation of the X_2 molecule, Θ_v the characteristic temperature of vibration of the X_2 molecule and ρ the nuclear spin weight (commonly taken as unity).

Expression of Q in terms of E_{ij} for O-site (octahedral interstices) occupations of X atoms in a face centred cubic (fcc) lattice and that in a body centred cubic (bcc) lattice are given as follows [10, 11]

$$Q(\mathrm{O/fcc}) = 6E_{X-M} \qquad (7)$$

$$Q(\mathrm{O/bcc}) = 2E_{X-M}^{(I)} + 4E_{X-M}^{(II)} - E_{M-M}^{(II)} \qquad (8)$$

where superscripts (I) and (II) to E_{X-X} and E_{X-M} for the bcc structure refer to first and second nearest neighbours (n.n.), respectively.

Analysis procedures might be as follows.

1. Obtain $D(X_2)$ at the temperature concerned from thermodynamic table (e.g. [12]).
2. Calculate $C(T)$ values (Equation 6).
3. Derive μ_X^0 at temperatures concerned by substituting values of $D(X_2)$ and $C(T)$ into Equation 5.
4. Prepare isothermal plots of A versus x on the basis of experimental P–T–C relations (Equation 2) providing θ, leading to linear A versus x.
5. Evaluate E_{X-X} at temperatures concerned from slopes of A versus x plots.
6. Determine K values at temperatures concerned from the intercept values of A at $x = 0$ (Equations 2 and 5).
7. Apply least mean squares treatment for the K versus T relation to determine values of Q and $R \ln f_X$ (Equation 2).

In the case of a very dilute interstitial solution where no n.n. solute–solute interaction arises, E_{X-X} must become zero [1–8, 10, 11, 13] and so A at a given temperature would become constant with x.

For some very dilute interstitial solutions, MX_x ($x \ll 1$), the value of θ fulfilling such a condition is easily determined [13] due to the occurrence of significant deviation of the A versus x isotherms from the constant relation by the choice of unrealistically small values for θ. The smallest value of θ leading to constant A values at a given temperature irrespective of x might be defined as the θ value for MX_x under consideration.

On the other hand, in other groups of very dilute interstitial solutions, the slope of A versus x isotherms is kept to virtually 0 for a very wide range of θ, and a clear definition of the threshold θ value leading to $E_{X-X} = 0$ is difficult. For such a system, K versus T relations (Equation 3) must be derived for different choices of θ and then the Q versus θ plot needs to be prepared (Fig. 1 of [4]; Fig. 2 of [11]). Q tends to converge towards a certain value as θ increased towards 1. Looking at such a plot, the threshold value for an intrinsic θ value for the very dilute interstitial solution MX_x might be vaguely defined.

As long as our concern is limited to the energy (enthalpy) term and the entropy term is outside our explicit consideration, it does not matter which θ value we take for the analysis from the range of values greater than the threshold θ value. Justification for this line of treatment is, roughly speaking, that the mode of statistical (random) distribution of X atoms over θ available interstitial sites in the M lattice in MX_x ($x \ll 1$) might be faithfully approximated under the choice of θ value in the range of values greater than the intrinsic value of θ (i.e. with a finer mesh than that corresponding to the intrinsic θ value) [4, 5, 11].

Because the group of solutions MX_x under consideration here are classified as very dilute interstitial solutions and their intrinsic values of parameter θ are difficult to specify uniquely, we undertake our calculations by taking $\theta = 0.5$, as was done for dilute solutions of hydrogen and nitrogen in iron in an earlier work [5]. By so doing, we derive reliable values for Q, but intrinsic values for the entropy parameter remain undetermined.

4. Results and discussion

The values of parameter Q derived for hydrogen and nitrogen solution in group VIa metals and those in iron-group metals, respectively, are summarized in Tables III and IV. Calculations undertaken for FeX_x systems were recalculations except for liquid FeH_x. Past calculation results for FeX_x are cited in Table IV in parentheses for comparison with the corresponding results obtained in this work, through analysis of compiled data in [9]. Corresponding Q parameters for α-FeH_x, α-FeN_x, γ-FeN_x and liquid FeN_x appear to be in satisfactory agreement (no more than 5 kJ mol^{-1} difference) between this work and past evaluations. This observation seems to imply that data compiled in [9] might be sufficiently reliable. However, the value of Q estimated in this work for γ-FeH_x is by about 15 kJ mol^{-1} less negative than the previous estimation [5]. The P–T–C data for γ-FeH_x reported by da Silva and McLellan [15] have been analysed [5]. Noting that da Silva and McLellan's experiment [15] was undertaken using high-purity iron, we decided to take the Q value for γ-FeH_x of -138 kJ mol^{-1} reported in the earlier work [5]. Relatively large discrepancies in Q values for δ-FeH_x and δ-FeN_x between this work and past estimations [5] (~ 50 kJ mol^{-1}) might arise from scarcity of P–T–C data points for these phases ([15] for P–T–C data of δ-FeH_x, and [16] for δ-FeN_x) analysed in the earlier work. However, noting that high-purity iron metal was used in the work of McLellan and co-workers [15, 16], the reliability of individual data points in their work might be high, although compiled data in [9] must represent trends correctly. As such, for the time being, it was felt difficult to judge which Q values must be taken eventually for δ-FeH_x and for δ-FeN_x.

In order to see the trends in the variation of Q values in a visualized manner, we plotted the results summarized in Tables III and IV, which were derived from the present analysis, in Fig. 1. In this figure, Q for molten CrN_x (-541 kJ mol^{-1}, Equation 27 in [4]) and that for molten MnN_x (-486 kJ mol^{-1}, Table 1 in [8]) derived in the earlier analyses were also plotted. As summarised in Table 1 in [8], on going from titanium to iron in order of increasing element group number of M, Q for molten MN_x became less negative (i.e. less stable nitrogen in molten M). Thus Q for

TABLE III Q-values estimated for solutions of hydrogen and nitrogen in group VIa metals on the basis of P–T–C relationships summarized in Table I with $\theta = 0.5$

MX_x					
M	State	X			
		H		N	
		Q (kJ mol^{-1})	T (K)	Q (kJ mol^{-1})	T (K)
Cr	Solid	− 130	1403–1003	− 410	1673–1073
		− 166	1003–773		
Mo	Solid	− 132	1773–1173	− 337	2673–1873
W	Solid	− 78	3273–2703	− 217	3323–2673
		− 153	2703–1873		
		− 84	2023–1173		

TABLE IV Q-values estimated for solutions of hydrogen and nitrogen in iron-group metals on the basis of P–T–C relationships summarized in Table II with $\theta = 0.5$. Q-values in parentheses refer to those estimated in earlier works; [11] for α-FeX_x (X = H, N): [5] for γ- and δ-FeX_x (X = H, N): [4] for liquid FeN_x

MX_x					
M	State	X			
		H		N	
		Q (kJ mol^{-1})	T (K)	Q (kJ mol^{-1})	T (K)
Fe	Liquid	− 144	1973–1809	− 432 (− 427)	2023–1809
	Solid bcc (δ)	− 151 (− 100)	1809–1664	− 414 (− 352)	1809–1673
	fcc(γ)	− 154 (− 138)	1664–1183	− 453 (− 455)	1673–1183
	bcc (α)	− 168 (− 171)	1183–473	− 416 (− 420)	1183–773
Co	Liquid	− 135	1973–1765	− 393	1973–1823
	Solid (fcc)	− 151	1765–1273	–	–
Ni	Liquid	− 155	1973–1773	− 391	1973–1823
	Solid (fcc)	− 171	1673–623	–	–

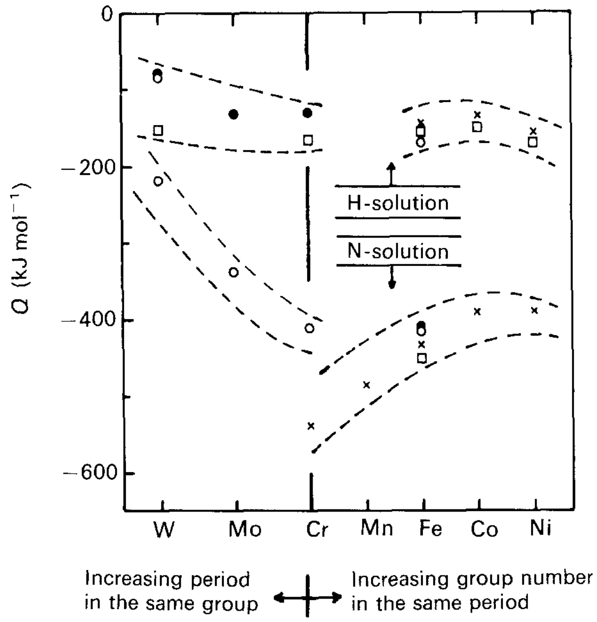

Figure 1 Plots of Q for hydrogen and nitrogen solution in group VIa and iron-group metals estimated by statistical thermodynamic analysis. (×) Q in the molten phase; (●, □, ○) Q in the solid phase in descending order of temperature range for stable existence (e.g. in the case of FeX_x, (●) refers to Q of the δ phase, (□) that of γ phase and (○) that of α phase).

molten CoN_x and molten NiN_x were obtained in this analysis. These values are comparable to each other, lying at a level slightly less noble than that for molten FeN_x.

The stability of hydrogen in iron-group metals in the molten state appeared to increase in the following order: molten CoH_x < molten FeH_x < molten NiH_x. This order appears to correspond well with the order of hydrogen solubility in these molten metals compared under comparable $p(H_2)$ and T (for a quick comparison, see, for example, [17], Fig. 3.14 and Table 3.7 for NiH_x, Table 12.42 for FeH_x and Table 12.43 for CoH_x). Thus, estimated values of Q for hydrogen solution in molten iron-group metals might be judged as acceptable.

There are three solid FeH_x phases; high-temperature bcc phase (δ), fcc phase (γ) and low-temperature bcc phase (α) in descending order of temperature. As shown in Fig. 1, the stability of hydrogen in condensed FeH_x phases tended to increase from one phase to another as temperature decreased.

Fig. 1 also shows that the stability of hydrogen in fcc phases of iron-group metals tends to increase according to the order: fcc CoH_x < fcc FeH_x < fcc NiH_x. This order of hydrogen stability for fcc phases of iron-group metals is comparable to that for molten phases.

Unlike the case for the order of hydrogen stability in an iron lattice, nitrogen stability in an iron lattice did not appear to vary monotonically according to the order of phases emerging with temperature; nitrogen in δ-FeN_x was the least stable and nitrogen in γ-FeN_x was the most stable.

Now, we look into variation patterns of Q for hydrogen and nitrogen solutions in group VIa metals (Cr, Mo and W). There were no P–T–C data available in [9] for these systems in the molten state except for molten CrN_x. Even for molten CrN_x, values of parameters, A and B [9] were given in Equation 1 to be 3.14 and − 2670, respectively, for the temperature range 1600–1900 °C whose validity range was limited to very dilute nitrogen solution regime in a molten chromium lattice. However, as presented by Ishii *et al.* [18], the range of nitrogen solubility in molten CrN_x is too extensive to be approximated as the very dilute nitrogen solution in a molten chromium lattice. Thus, as described above, we plotted Q for molten CrN_x as the value − 541 kJ mol^{-1} estimated in the earlier work [4] through analysis of data reported by Ishii *et al.* [18, 19]. Analysis of P–T–C data for molten CrN_x presented in [9], assuming a very dilute solution, yielded $Q = -488$ kJ mol^{-1}, which deviated significantly from − 541 kJ mol^{-1}.

As given in Table III, Q for the primary solid solution CrN_x was estimated to be − 410 kJ mol^{-1}. Thus, it appears that nitrogen in primary solid solution CrN_x is less stable than in molten CrN_x phase.

According to earlier analysis for a hypo-stoichiometric sub-nitride of chromium [14, 19], Q for the Cr_2N phase was estimated to be − 849 kJ mol^{-1}.

This might give the impression that nitrogen atoms in the Cr_2N phase are incomparably more stable than those in CrN_x primary solid solution. However, we should not forget that intense repulsive N–N interaction exists in the Cr_2N phase, while in primary solid solution CrN_x the N–N interaction might be assumed to be negligible. Q refers to the extent of stabilization of the interstitial atom through formation of X–M bonds in MX_x alone, as definition of Q (Equation 4) indicates. Thus, when compared in terms of crystal lattice energy as a whole, the stability of Cr_2N phase and that of the primary solid solution CrN_x might not be so much different, as represented by the large difference in Q values between these two phases.

Fig. 1 shows that the stability of nitrogen in the solid phase of group VIa metals tends to decrease rapidly as the number of the period increased. No such drastic variation in Q was ever found for a given interstitial element for the metals within the same group in the Periodic table (cf. Fig. 2 in [1]). Therefore, re-calculations might be desirable for these systems.

P–T–C relations for primary solid solution WH_x were given in three different forms according to temperature, as summarized in Table I [9]. This implies that phase changes such as those observed for iron ($\alpha \rightarrow \gamma \rightarrow \delta$ in ascending order of temperature) might take place for the tungsten lattice. In Fig. 1, we mark Q for the WH_x phase existing in the temperature range 2430–3000 °C (high-temperature phase) with ●, that for WH_x in the range 1600–2430 °C (medium-temperature phase) with □, and that for WH_x in the range 900–1750 °C (low-temperature phase) with ○. Q for the low-temperature phase of WH_x and that for the high-temperature phase are comparable to one another, lying at a level slightly less negative than that of the medium-temperature phase.

For WH_x in the medium-temperature range, Q appears to be comparable to values for MoH_x and CrH_x. Two Q values were enumerated for CrH_x primary solid solution according to the temperature ranges but they did not differ much from one another, unlike the case with WH_x. Looking at Fig. 1, it might be said that hydrogen in primary solid solutions in group VIa metals tends to become less stable as the number of the period increased.

5. Conclusion

Results of analysis of P–T–C data for hydrogen and nitrogen solutions in iron-group and group VIa metals compiled in [9] in a normalized format as represented by Equation 1 on the basis of statistical thermodynamics, are summarized.

Judging from a comparison of the present analysis results for FeX_x with available analysis results for corresponding systems [4, 5, 11], the data compiled in [9] appeared to be sufficiently reliable.

Observed trends in Q for different systems as a whole appeared to be acceptable, whereas some systems seem to deserve re-analysis to derive convincing values of Q.

Several types of atom cluster models in $Fe_{1-y}M_yN_x$ were developed [1, 4, 6–8] and values of parameters, E_{N-Fe} and E_{N-M}, in $Fe_{1-y}M_yN_x$ appeared to be roughly approximated as the corresponding values in FeN_x and MX_x [4, 6, 8]. Similar atom clustering might take place in $Fe_{1-y}M_yH_x$ and similar arguments as for E_{N-M} might be valid for E_{H-M} parameters. Now that E_{X-M} parameters have been evaluated for hydrogen and nitrogen solution in iron-group and group VIa metals, it might be worth trying to simulate P–T–C relations for a dilute solution range of X (= H, N) in the $Fe_{1-y}M_y$ lattice for which values of E_{X-M} parameters are known, as the next step.

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