Interaction of chromium with solute carbon and solute nitrogen in iron
鉄中の固溶炭素・固溶窒素とクロムの相互作用

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1. Introduction

Quantitative knowledge on interaction between alloying elements and C and N in iron is important in steelmaking and in controlling the properties of engineering steels. Effects of tertiary components on the solubility of carbon and that of nitrogen in molten iron were extensively studied in the 1950s, and the accumulated data of 'interaction coefficient' [1] have been utilized in producing, for example, high purity steels. For solid phases, effects on the solubilities of C and N in γ iron were also studied for some important alloying elements such as Mn, Cr, and V, together with solubility products [1]. For α iron, on the other hand, much fewer data are available, and not many of them are reliable, even though the interaction between the solute species plays critical roles in properties of ferritic steels. The experimental difficulties for α iron are (1) very limited solubilities of C and N, and (2) slow kinetics, which requires a long time to attain true equilibrium.

We have been studying the interaction between the interstitial (i) solutes (C and N) and alloying elements, most of which are substitutional (s) solutes, in α iron through the influence of the latter on the Snoek relaxation of the former [2, 3, 4]. The Snoek relaxation is a well-known anelastic relaxation effect due to stress-induced diffusional motion of the interstitial solute atoms [5]. If the substitutional solute atom affects the potential energies of the interstitial sites around it, the rates of diffusional jumps of the interstitial solute atom become different from those in unalloyed iron. This can be used conversely to evaluate of the interaction between the i and s solute atoms, or 'i–s' interaction [6]. This method does not suffer much from the two difficulties mentioned above: the mechanical relaxation can sensitively detect C and N of concentrations as low as 10 at. ppm, and the method is to observe single atomic jumps of C and N in the paraequilibrium state distributed in the host alloy crystal.

In a previous work we studied the interaction between N and Cr in α iron studied by measuring the Snoek relaxation in a series of dilute Fe–Cr–N alloys [3, 4]. We continue to work on the important alloying element Cr; in the present paper we report the interaction between C and Cr studied by the same method. In this study, in addition, we have evaluated the N–Cr and C–Cr interactions by the thermochemical method, which was employed in many of the past studies on liquid iron and γ iron mentioned above: measuring the dependence of the equilibrium solubility of C or N on the concentration of Cr. We discuss how these two experiments compare with each other in theory and in practice.

2. Interaction coefficient and interaction energy

Traditional work on evaluating the interaction between different components is based on Wagner's theory of the thermodynamics of multicomponent solutions [7]. Here we show the relation between the thermodynamic interaction coefficient and the atomistic interaction energy [8, 9, 10, 11], which are the central parameters characterizing the influence of the tertiary element on the solubility and atomic jumps, respectively, of the interstitial solute.

In multicomponent alloys, the activity of component i in the solution, which can be written as

$$a_i = \gamma_i x_i \qquad (1)$$

for dilute solutions, where γ_i is the activity coefficient and x_i is the concentration (mole fraction) of i. The interaction coefficient, which describes the influence of component j on the activity of i, is defiend as

$$\varepsilon_i^{(j)} \equiv \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{x_i, x_j \to 0}, \qquad (2)$$

where x_j is the concentration of j. This can be evaluated by measuring the equilibrium solubility (not the solubility limit) of i under an identical activity of i in a series of dilute alloys differing in the concentration of j. For dilute solutions where the effect of j can be approximated as linear on concentration, the activity may be expressed as

$$\ln \gamma_i = \ln \gamma_i^\circ + \varepsilon_i^{(j)} x_j, \qquad (3)$$

where γ_i° is the activity coefficient in the absence of j. In this case, the effect of j on the equilibrium solubility is written as

$$x_i = x_i^\circ \exp\left(-\varepsilon_i^{(j)} x_j\right). \qquad (4)$$

The procedure of evaluation described above is evident from this expression. When $\varepsilon_i^{(j)}$ is negative, for example, the solubility of i is increased by the addition of j, indicating attractive interaction.

To connect the phenomenological thermodynamics to an atomistic theory, we consider variations of the potential energies for the interstitial solute atom, 'i', around a substitutional solute atom, 's', as shown in Fig. 1. For simplicity we assume that only the energy of the interstitial site closest to the s atom is changed by ΔE. Generally the energies at farther sites may be influenced as well as the saddle-point energies, but we consider here a model with only two distinct sites, referred to as a two-level system. The i atoms distribute over the two groups of sites, one with a lower energy (trap sites) and the other, normal sites, with fractions depending on the energy and population of the trap sites. By applying Fermi–Dirac statistics to the distribution, a relation between the chemical potential μ_i ($= kT \ln a_i$) and the interaction energy ΔE can be derived. Then the expression for the interaction coefficient is obtained from Eq. (2). The result is

$$\varepsilon_i^{(j)} = \frac{z}{m}\left[1 - \exp\left(-\frac{\Delta E}{kT}\right)\right]. \qquad (5)$$
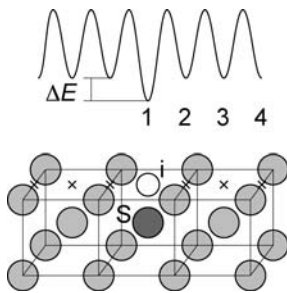
Fig. 1   Bottom: An interstitial solute atom 'i' at the nearest neighbour octahedral interstitial site of a substitutional solute atom 's' in a body-centred cubic crystal. Cross symbols indicate farther interstitial sites. Top: Profile of the potential energy for the 'i' atom. Numbers indicate the classification of the sites according to the distance from the 's' atom.

Here, z is the number of trap sites per 's' atom, m is the number of interstitial sites per host atom site (3 for octahedral interstitial sites in a bcc crystal), k is Boltzmann constant, and T is temperature.

3. Experimental procedure

3.1. Materials

Pure iron and the five dilute Fe-Cr alloys were used in this work. The alloys prepared from high purity iron and chromium by argon arc melting. Their nominal compositions are 0.3, 0.6, 0.9, 1.2, and 1.8 at. % Cr, and the Cr concentrations analysed by the inductively-coupled plasma analysis are 0.24, 0.60, 0.85, 1.20, and 1.77, with error margins of ± 0.01, all in at. %. Wires of 1 mm in diameter and 50 mm in length were prepared by cold-rolling and drawing from button-shaped ingots. To eliminate deformation textures possibly formed by the cold-work, the wires were annealed at 1223 K (above the $\alpha \leftrightarrow \gamma$ transformation temperature) for 1 h in a vacuum. The wires were then subjected to annealing in an atmosphere of wet hydrogen (hydrogen gas of 1 atm fed through water of 310 K) at 973 K for 24 h. The DC electrical resistivity and the Snoek relaxation proved that the contents of C and N were reduced to below the detectable limit, a few at. ppm, by this treatment.

3.2. Nitriding and carburizing

Either nitrogen or carbon was introduced to the hydrogen-treated wires by placing them in a flow of a mixture of high purity hydrogen and ammonia or methane [12, 13, 14]. The total pressure was 1 atm and the flow rate was about 200 ml min^{-1}. The activity of nitrogen or carbon was controlled by the proportions of the gas components and temperature. A typical setting was 98% hydrogen and 2% ammonia, 96% hydrogen and 4% methane. The absolute flow rate was electronically regulated within ± 1 ml min^{-1} but was different each time by 10 or 20 ml min^{-1}, for the sake of conveniently specifying the desired proportions of the gas components.

3.3. Mechanical relaxation measurements

Mechanical loss at small strains was measured using a low-frequency inverted torsion pendulum instrument by the free-decay method. The resonance frequency and the logarithmic decrement were measured with an initial strain amplitude of 10^{-5}, while temperature was changed continuously with

time. The frequency of vibration was about 1 Hz. To suppress magnetomechanical damping, a static magnetic field of 1.6×10^4 A m^{-1} was applied in the direction parallel to the wire axis.

4. Results and discussion

4.1. Effect of Cr on solubility of N

Wire samples of 0Cr, 0.3Cr, 0.6Cr, and 0.9Cr, were nitrided at 836 K for 11.5 h under three different N activities, (1) 2.69×10^{-4}, (2) 3.96×10^{-4}, and (3) 5.13×10^{-4}. The hydrogen : ammonia proportion was 990 : 10, 985 : 15, and 980 : 20, respectively. The nitriding time was chosen to realize almost uniform distribution of N in the wire sample: it was taken as twice the time required for the diffusion of N atoms to raise the concentration at the centre of the wire to 95% of the concentration at the surface.

The N contents of the nitrided samples were analysed by combustion method. The results are shown in Fig. 2. This diagram indicates the enhancement of the solubility by Cr that conform to Eq. (4). The N concentrations attained are all well below the solubility limit of N against the precipitation of Fe$_4$N in unalloyed iron at 836 K, which is over 3,000 at. ppm [15]. In the presence of Cr, however, the solubility limit is reduced: it is about 800 at. ppm for 0.9 at. % Cr at 836 K according to the solubility product of Cr and N reported by Imai et al. [16]. The uppermost point in Fig. 2 is close to but still lower than this limit. We thus assume that in none of the samples occurred precipitation of nitrides; they are of single-phase solid solution. The smooth variations of the solubility on the Cr concentration seem to support the assumption.

The same data are plotted against the activity a_N in Fig. 3 (a). A straight line can be drawn from the origin for each of the data points from the same Cr concentration. In reference to Eq. (1), the slope of the line is the reciprocal of the activity coefficient γ_N. Its values are then plotted agains Cr concentration x_{Cr} in Fig. 3 (b). The four points from the four Cr concentrations form a straight line, as expected from Eq. (2). By linear regression, the slope, which is the interaction coefficient $\varepsilon_N^{(Cr)}$, is determined to be -58.5 ± 3.2. This is similar in magnitude to those reported previously by the same method by Taneike and Okamura but the error range is much smaller.
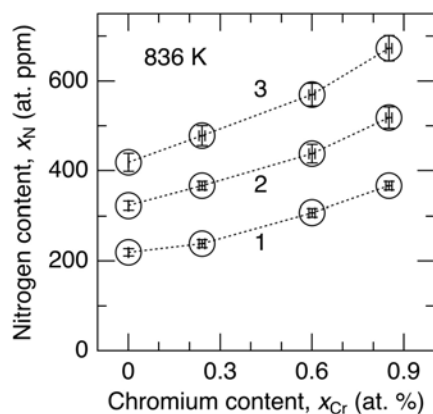

Fig. 2 Concentrations of N in pure iron and dilute Fe–Cr alloys nitrided at 836 K. Curves 1, 2, and 3 are those from the three sets nitrided under the N activities described in the text.
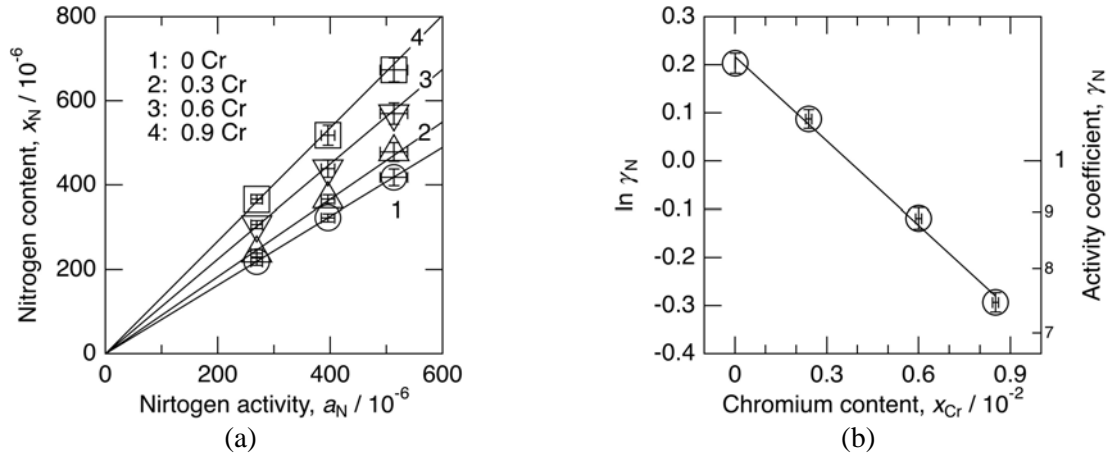
Fig. 3   (a) The same data as Fig. 2 plotted against N activity, and (b) the activity coefficient of N as a function of Cr concentration.

The interaction energy is given from the interaction coefficient by inverting Eq. (5):

$$\Delta E = -kT \ln\left(1 - \frac{m}{z}\varepsilon\right). \tag{6}$$

If the first nearest neighbour octahedral sites to the 's' atom are the low-energy positions (i.e., trap sites), z is 6. It is 12 for the second neighbour sites, and 18 if both the first and the second neighbour sites are similar trap sites. The values of ΔE derived from the interaction coefficient are listed in Table 1, together with those reported by Guan et al. [4] by analysing the influence of Cr on the Snoek relaxation of N for Cr concentrations up to 0.2 at. %. The two sets of evaluations agree only if both the first and second nearest neighbour sites are assumed to be trap sites of similar importance. However, since the Snoek relaxation is measured at temperatures around 300 K, attention should be paid to possible effects of temperature on the interaction energy; it is not guaranteed if ΔE could be regarded constant for the range of temperatures.

Table 1   Interaction energy ΔE between N and Cr in α iron evaluated from the solubility [this work] and from the Snoek relaxation [4].

Trap site*	ΔE / eV	
	From solubility at 836 K [This work]	From Snoek relaxation [4]
1	-0.246 ± 0.004	-0.180
2	-0.198 ± 0.004	-0.165
1 and 2	-0.171 ± 0.004	1: -0.17 2: -0.14

* 1: first nearest neighbour octahedral sites, 2: second nearest neighbour octahedral sites.

4.2. Effect of Cr on solubility of C

Samples of 0Cr, 0.6Cr, 1.2Cr, and 1.8Cr were carburized at 998 K for 4.5 h, aiming at C contents of about 100 at. ppm and 200 at. ppm, in a flow of hydrogen and methane composed of 197 : 3.1 and 173 : 9.1, respectively. The concentrations of Cr of the alloys used are twice as high as those for nitriding, since previous studies [17, 18] suggested weaker influence of Cr on C than on N.

The C contents analysed by combustion method are shown in Fig. 4. In contrast to the case of N (Fig. 2), the amounts of C absorbed in Fe–Cr alloys are virtually equal to that in unalloyed iron. As the C concentration is independent of interaction within the experimental errors, we conclude that the interaction coefficient $\varepsilon_C^{(Cr)}$ is essentially zero, and so is the interaction energy ΔE.
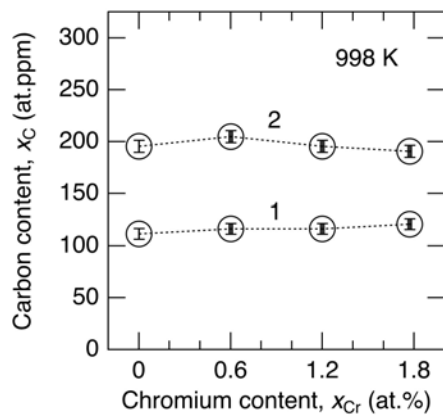

Fig. 4   Concentrations of C in pure iron and dilute Fe–Cr alloys nitrided at 998 K. Curves 1 and 2 are those from the two sets carburized under the two conditions described in the text.

Wada [19] made a similar experiment on a series of Fe–Cr alloys up to 8.7 at. % Cr at 985 K and obtained –72 ± 2 as the value the interaction coefficient. It yields –0.31 to –0.22 eV (for z = 6 to 18) for the the interaction energy, which is larger in magnitude than the present result on N–Cr. Nishizawa et al. [20] attempted to evaluate the interaction coefficient using a 'diffusion multiple', which is a set of diffusion couples connected in series, of Fe–Cr–C alloys differing in Cr concentration. During annealing carbon atoms redistribute over neighbouring sections by diffusion, while Cr atoms are much less mobile, so that paraequilibrium is realized. By analysing the C concentration in an annealed multiple, which is not uniform but is a function of the local concentration of Cr, they obtained the effect of Cr solubility of C, indicating attractive interaction with ΔE of about –0.2 eV. In view of the present result, these data in the literature appear too large in magnitude. A possible origin of this discrepancy is clustering of Cr atoms driven by the presence of C atoms, i.e., to form clusters consisting of quite a few atoms of Cr and C.

Recent experiments on the Snoek relaxation of N atoms in Fe–Cr alloys containing larger amounts of N strongly suggest that such clustering does occur [21]. It is a gradual, or stepwise transition from ideal paraequilibrium (in which the distribution of Cr solutes is frozen) to orthoequilibrium. The transition is to proceed significantly if the annealing time is inappropriately long. This could be the case for the experiments of Wada and Nishizawa et al., who both held the samples at the equilibration

temperature for a much longer time than in the present experiment, more than 100 hours. A variety of metastable solute-atom clusters may appear during the transition, and the effective interaction energy would vary depending on the nature of the clusters. To determine the interaction energy between a single 'i' and 's' solute atoms, or the formation energy of an isolated i–s atom pair, experimental conditions should be carefully set up to avoid formation of those higher order solute-atom clusters.

4.3. Effect of Cr on Snoek relaxation due to C

The wire samples carburized at 998 K were solution-treated at the same temperature for 45 min using a vertical vacuum furnace and were quenched into oil of 273 K without breaking the vacuum. Each of the samples, of supersaturated solid-solution, was mounted to the torsion pendulum instrument, cooled down to 150 K and then the mechanical loss and resonant frequency were measured as a function of temperature by heating or cooling at a rate of 1 K min^{-1}.

Figure 5 shows the results of the measurements for samples containing about 110 at. ppm C. Unlike the case of Fe–Cr-N alloys [3, 4], effects of Cr on the Snoek relaxation is hardly discernible. The results for the other set of samples, with 200 at. ppm C, were essentially the same.
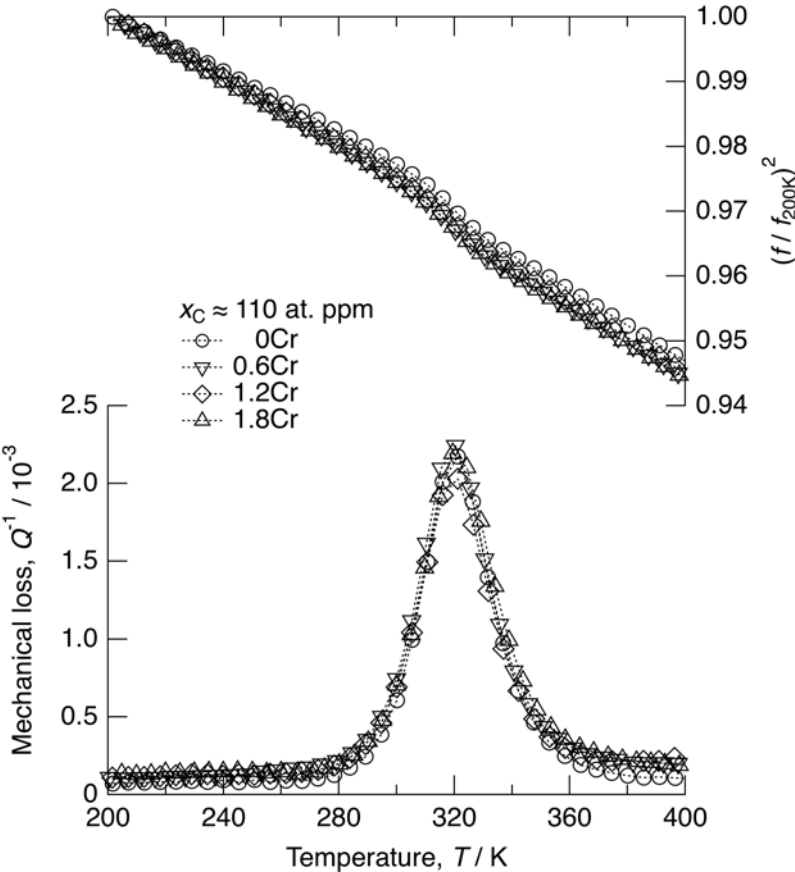

Fig. 5   The mechanical loss Q^{-1} (lower) and the square of the resonance frequency f of carburized samples containing 110 to 120 at. ppm C. The frequency is normalized to the value at 200 K.

These results are in agreement with the previous study [18] carried out for lower Cr concentrations

employing the same method of carburizing. This indicates that the interaction between C and Cr in α iron is very weak, and is consistent with the little influence on the C solubility. It was reported, on the other hand, that addition of Cr did not give rise to a new component in the relaxation profile but systematically reduced the relaxation strength [22]. We suspect that solute atom clusters were developed, as the samples were prepared by decarburization from materials containing larger amounts of C through extended heat treatments. Similar trend (lower relaxation strength in alloys of higher Cr concentrations) was in fact observed in the present experiment for the second set of samples containing about 200 at. ppm C. It is possible that the higher concentration of C promoted formation of Cr–C atom clusters.

5. Conclusions

The effects of Cr on the equilibrium solid solubility on N and C in α iron have been studied by the standard thermochemical equilibration method, by subjecting a set of dilute Fe–Cr alloys in a flow of gas mixture (hydrogen and ammonia, and hydrogen and methane, respectively). The results are summarized as follows:

(1) The addition of Cr up to 0.9 at. % appreciably increases the solubility of N at 836 K, and the effect can be described by Wagner's theory with the interaction coefficient $\varepsilon_N^{(Cr)} = -58.5 \pm 3.2$. The interaction energy ΔE is estimated to be –0.17 to –0.25 eV, depending on the trap sites assumed. This result agrees fairly well with the evaluation from the effect on the Snoek relaxation in dilute Fe–Cr-N alloys [4].

(2) No significant effect of Cr was observed on the solid solubility of C at 998 K for Cr concentrations up to 1.8 at. %, and the same is true for the Snoek relaxation for solution-treated Fe–Cr–C alloy samples.

Since Cr is one of the carbide forming elements in iron, such a weak interaction of Cr and C was unexpected and is against the common knowledge established for liquid iron and γ iron. More experiments are desired to ensure this finding, with different carburizing conditions, pre- and post heat treatments, deliberate long-time ageing for cluster evolution, as well as direct observation of nano-scale microstructures by TEM or atom-probe.

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