Interaction between interstitial and substitutional solute atoms in iron

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Abstract: Theoretical and experimental aspects of the effects of alloying elements on the behaviour of C and N dissolved in iron are reviewed, focussing on methods of evaluating the interaction between the interstitial and substitutional solute atoms. With the simple trap model in a two-level system, the standard method of measuring the equilibrium solubility and the Snoek relaxation can be utilized to determine the interaction energy, although there are practical difficulties for α iron. This method of approach has given reasonable attractive interaction of N–Cr pairs, but suggests very weak interaction between C and Cr. Possible origins of this interesting difference are discussed.

1. INTRODUCTION

In structural ferritic steels, alloying elements change the properties of the material most often by interacting with carbon or nitrogen, thereby affecting the behaviour of the interstitial solute atoms. The roles of the micro-alloying elements such as V, Nb, and Mo are typical examples: driven by chemical attraction, they form solute-atom clusters or small carbide/nitride precipitates, which give rise to significant improvements in strength. Influences of alloying elements on the behaviour of C and N are important also in steelmaking, so that the solute–solute interaction in molten iron has been extensively studied since the 1940s. The parameter characterizing the interaction, the interaction coefficient, has been evaluated for a number of alloying elements, by measuring their effects on the equilibrium solubility of C or N [1]. Similar evaluations have been made for austenite [1-3]. In contrast, studies on the interaction in ferrite are scarce, and reliable data are still very limited, despite its importance. Experimental investigation of α iron is difficult because the solubility limits of C and N are extremely low.

Interaction between interstitial C or N and substitutional (s) solute atoms, or i–s interaction, was also known for α iron already in the 1950s: alloying elements such as V, Cr, and Mn modify the characteristic mechanical loss due to stress-induced reorientation jumps of interstitial C/N atoms (the Snoek relaxation) [4, 5]. It was evident that the phenomenon was caused by association of the interstitial solute atoms with the substitutional solute atoms, or 'trapping' of the former by the latter [6-8]. The i–s interaction was addressed in a classic monograph published in 1980 [9] as one of the important factors in microstructure formation and properties of steels, even though not much information was available at that time. Knowledge has been accumulated in the last three decades but is yet mostly phenomenological and qualitative [10].

To establish a scientific basis for better and quantitative understanding of the solute–solute interaction, we have developed a theoretical framework and experimental methods for accurately determining the interaction energy. In this paper, first we discuss theoretical aspects of the effects of substitutional solutes on the solubility and diffusion of the interstitial solutes. Next we show recent results on the interaction of some transition-metal elements with C and N. The i–s interaction in bcc iron turns out to be similar to those in fcc and liquid iron for some combinations but not for some others.

2. MEASURES OF SOLUTE–SOLUTE INTERACTION
2.1. Interaction coefficient

In a multi-component solution, the effect of solute species j on the thermodynamic activity of species i is described by the interaction coefficient,

$$\varepsilon_i^{(j)} = \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{x_i, x_j \to 0}. \tag{1}$$

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Here, γ_i is the activity coefficient of i, and x_i and x_j are mole fractions of i and j, respectively [10, 11]. Using the interaction coefficient, the activity coefficient and the equilibrium solubility of i may be expressed respectively as

$$\gamma_i = \gamma_i^\circ \exp\left(\varepsilon_i^{(j)} x_j\right),$$ (2a)

$$x_i = x_i^\circ \exp\left(-\varepsilon_i^{(j)} x_j\right),$$ (2b)

where γ_i° and x_i° are the activity coefficient and the solubility of i in the absence of j.

Most of the experimental data of ε for C–solute and N–solute interaction in molten iron and γ iron have been obtained by measuring the variations of the equilibrium solubility by the addition of the alloying element j on the basis of Eq. 1. In practice, a series of dilute alloys with different concentrations of j are equilibrated with C or N of a defined activity, and the resultant concentrations x_i (the equilibrium solubility in the single phase primary solution) are measured. With a few set of data obtained at different activity levels, one can determine the dependency of the activity coefficient γ_i on the concentration of the alloying element x_j. The interaction coefficient can then be derived by analysing the dependency in terms of Eq. 1. It is also possible to evaluate $\varepsilon_i^{(j)}$ by simply applying Eq. 2b to a single set of experimentally determined relation between x_i and x_j. The former procedure is preferred for accurate evaluation.

2.2. Interaction parameter and interaction energy

In the regular solution model of multi-component solutions [2-3], the activity coefficient of component i in the presence of component j is expressed as $\gamma_i = \gamma_i^\circ \exp[(W_{ij}/RT) x_j]$ with the interaction parameter W_{ij}. The interaction coefficient is therefore given as

$$\varepsilon_i^{(j)} = \frac{W_{ij}}{RT}.$$ (3)

From the microscopic viewpoint, the origin of the interaction may be envisaged as illustrated in Fig. 1: one (or some) of the positions for the interstitial solute atom (open circle) may be different in energy in the vicinity of the substitutional solute atom (dark grey circle) from those distant from it. Such positions, characterized by the difference in energy ΔE, define either *trap* or *anti-trap* sites depending on its sign, and lead to an inhomogeneous distribution of the interstitial solute atoms in otherwise homogeneous single-phase solution. If there are only one type of trap sites, this is the problem known as a two-level system in statistical mechanics. In this framework, the following relation can be derived when $x_i \ll x_j \ll 1$ [12, 13]:

$$\varepsilon_i^{(j)} = \frac{z}{m}\left[1 - \exp\left(-\frac{\Delta E}{kT}\right)\right].$$ (4)
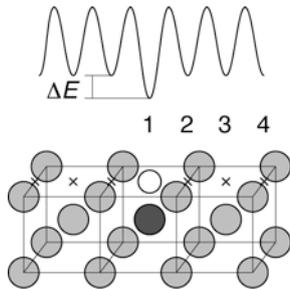

Fig. 1 Schematic illustration of the potential energy profile around a substitutional solute atom (dark grey circle) for an interstitial solute atom (open circle) occupying octahedral sites in a bcc crystal. The numerals 1 to 4 indicate the first to the fourth neighbour octahedral sites. Host (solvent) atoms are illustrated as light grey circles.

Here z is the number of the trap (or anti-trap) sites per substitutional solute atom, and m is the number of the interstitial sites per solvent atom, which is given by the geometry of the crystal. If the octahedral interstitial sites closest to the substitutional solute atom are the trap sites, for example, z/m is equal to $6/3 = 2$ for the bcc structure and $6/1 = 6$ for the fcc structure, respectively.

If the interaction is weak in comparison to thermal energy, $|\Delta E/(kT)| << 1$, Eq. 4 can be modified to an approximate expression, $\varepsilon_i^{(j)} \approx (z/m)\Delta E/(kT)$. By combining this expression with Eq. 3, we find $(z/m)\Delta E \approx W_{ij}/N_0$, where N_0 is Avogadro's number. Note, however, that this relation may not be valid for C and N in iron, for their interaction energy ΔE with common alloying elements is often of the order of 0.1 eV ($\approx$ 10 kJ mol^{-1}), while kT is even smaller at temperatures of interest.

3. EFFECTS OF ALLOYING ELEMENTS ON THERMODYNAMIC AND KINETIC PROPERTIES OF INTERSITITAL SOLUTES

3.1. Effect of alloying elements on the solubility

As mentioned above, the influences of alloying elements on the solubilities of C and N in liquid iron and γ iron were studied extensively in the past. Experimental values of the interaction coefficient reported in the literature by the year 2000 were collected by the present author and were made into a database [1]. Inspection of the data reveals that the interaction of transition elements with C and N is generally attractive for those located on the left-hand side of iron in the periodic table, and the strength of the attractive interaction, indicated by negative $\varepsilon_i^{(j)}$ and W_{ij}, is more pronounced for those which are farther off from iron. On the other hand, the interaction of elements located on the right-hand side appears repulsive [2-3].

For quantitative comparison and detailed discussion, both the interaction coefficient and the interaction parameter are inconvenient, as their values change significantly with temperature. Figure 2 shows the case of C–Cr [1]. The values of $\varepsilon_C^{(Cr)}$ and W_{CCr} of the three phases, each of which are negative, decrease their magnitude with increasing temperature. In contrast, the values of ΔE derived from $\varepsilon_C^{(Cr)}$ by inverting Eq. 4 is found to be rather insensitive to temperature. In Fig. 2, it is almost constant in each phase, about –0.20 eV in the α phase, –0.10 eV in the γ phase, and –0.06 to 0.08 eV in the liquid phase. These numbers may be taken as a basic parameter representing the strength of interaction. Note that ΔE is to be regarded as the difference in the *free energy* between trap sites and ordinary sites (but excluding the configurational entropy), so that it can also be temperature-dependent; it is only less sensitive than ε and W.
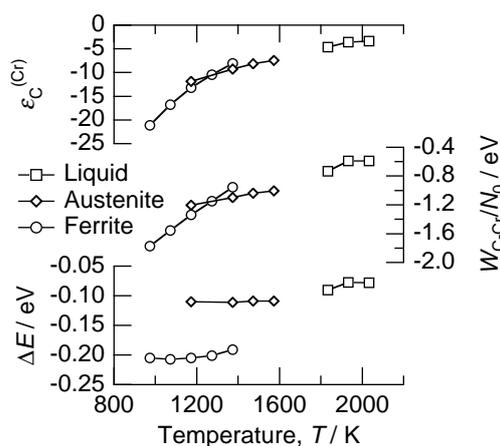

Fig. 2   Parameters characterizing the interaction between C and C: the interaction coefficient $\varepsilon_C^{(Cr)}$, the interaction parameter W_{C-Cr}, and interaction energy ΔE.

3.2. Effect of alloying elements on diffusion coefficient

Trapping of interstitial solute atoms caused by attractive interaction with much less mobile defects gives rise to not only increase in the solubility of the interstitial solute species but also slowing

down of diffusion, as known for hydrogen dissolved in metals [14]. The rate of macroscopic diffusion of the interstitial solute atoms is lowered because they stay for longer times at the trap sites. With the same model of trapping in the two-level system, the diffusion coefficient of the interstitial species i is expressed as

$$D_i = D_i^{\circ} \frac{1}{1 - \dfrac{z}{m} x_j + \dfrac{z}{m} x_j \exp\left(-\dfrac{\Delta E}{kT}\right)},$$ (5)

where D_i° is the diffusion coefficient in the absence of the tertiary species j acting as the trapping centre. Note that $(z/m) x_j$ is the concentration of the trap sites and $1 - (z/m) x_j$ is that of the ordinary sites. If the interaction is attractive, ΔE is negative and thus the factor $\exp[-\Delta E/(kT)]$ increases with decreasing temperature, resulting in progressive downward deviation of D_i from D_i°. Figure 3, which is a model calculation for C in α iron, illustrates this effect.

In practice, however, evaluation of the interaction from diffusion experiments is not easy in general. If the concentration of the substitutional solute species j is 1 at.% ($x_j = 0.01$), as in Fig. 3, the denominator in the right-hand side of Eq. 5 is not much larger than unity: for example, at 1000 K it is 1.04 for $\Delta E = -0.1$ eV, and 1.18 for $\Delta E = -0.2$ eV. This factor is in fact identical to the effect on the solubility in an approximate expression

$$x_i = x_i^{\circ}\left[1 - \frac{z}{m} x_j + \frac{z}{m} x_j \exp\left(-\frac{\Delta E}{kT}\right)\right],$$ (6)

which can be derived from Eq. 2b for the case where $|\varepsilon_i^{(j)} x_j| \ll 1$. Differences in the concentration of C or N by 10%, for example, 10 at. ppm out of 100 at. ppm, are distinguishable by chemical analyses using modern instruments, but those in the diffusion coefficient of this order of magnitude cannot always be detected, as they are usually within the range of experimental uncertainties. In fact, influences of alloying elements on the diffusion of C and N are reported to be small or not appreciable in the literature [15-17].
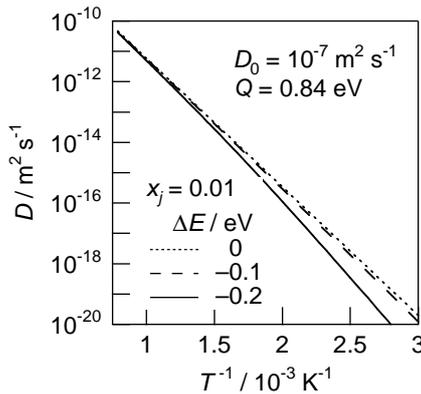

Fig. 3 Effect of trapping by substitutional solute species j on the diffusion coefficient of interstitial solute species i expected from Eq. 5. x_j is the concentration of species j. The Arrhenius parameters of the diffusion coefficient, pre-exponential factor D_0 and the activation energy Q, are those of C in bcc iron.

3.3. Effect of alloying elements on atomic jumps

The Snoek relaxation is an anelastic relaxation due to stress-induced reorientation of interstitial solute atoms occupying octahedral sites in a bcc crystal, which is controlled by jumps of the solute atoms between neighbouring interstitial sites, viz., the elementary process of their diffusion. As described briefly in Introduction, influences of small amounts of some alloying elements on the Snoek relaxation of C and N in iron were noticed as early as in the 1950s. For N, in particular, the ordinary relaxation peak is reduced, or sometimes suppressed, by the addition of such solute atoms as V, Cr,

Mn, Si, and a new relaxation appears at a temperature higher than the original one (when measured as a function of temperature under constant frequency). Similar effects have been observed for light elements in other bcc metals, e.g., O and N in V, Nb, and Ta [6, 18]. If the substitutional solute atom affects the potential energies of the interstitial sites around it as illustrated in Fig. 1, the rates of diffusional jumps of the interstitial solute atom must be different around there from elsewhere. This effect can be used conversely, in principle, to extract quantitative information on the interaction, on the basis of a theoretical model connecting the two-level system and the spectrum of the Snoek relaxation in the dilute ternary alloy.

One of such theories was first proposed by Meijering [19] and was developed by Koiwa [20-24]: it is to formulate the kinetics controlling the redistribution of the interstitial solute atoms over the octahedral sites around the substitutional atom, and to calculate the relaxation spectrum expected for an assumed set of jump rates of the interstitial solute atom by solving the set of rate equations. The jump rates between the non-equivalent interstitial sites, which depend on the distance from the substitutional solute atom, may be defined in terms of the frequency factor and the activation energy by assuming Arrhenius' expression. The latter can be conveniently given by specifying a potential energy profile, viz., site energies and saddle-point energies around the substitutional solute atom, in which ΔE is included. By calculating a theoretical spectrum and comparing it with the experimentally observed spectrum, one may find a potential energy profile that well reproduces the latter. Another method is to analyse the complex relaxation spectrum consisting of multiple relaxation components in terms of *normal modes* of relaxation. It is based on a group-theoretical method developed by Nowick [25-28], by which a complex spectrum can be decomposed into several standard Debye relaxations whose relaxation rates are given by linear combinations of various atomic jump rates. The two methods are equivalent, as discussed by Koiwa [21].

Analysing the relaxation spectrum on the basis of these theories is not straightforward, however, as it can be accomplished only by trial-and-error comparison. Moreover, one usually needs to determine more than one parameter even if there is only one type of trap sites, since the activation energy of the atomic jump is given by the difference between the site energy and the saddle-point energy. This method of analysis is nevertheless feasible and has in fact served to quantitatively discuss and accurately determine ΔE of C or N and some alloying elements in iron [29-31]. Experimental investigation of C and N in α iron is inherently difficult because the solubilities are very limited and long annealing times required for attaining thermal equilibrium in comparison to those in γ and liquid phases. The Snoek relaxation does not suffer much from these difficulties because it can sensitively detect C and N of concentrations as low as 10 at. ppm, and measurements are made in a supersaturated solution in a paraequilibrium state, which can be established quickly by redistribution of the fast diffusing interstitial solute atoms.

4. INTERACTION BETWEEN N AND C WITH CHROMIUM IN ALPHA IRON

By making use of the sensitivity of the Snoek relaxation, we studied the interaction of N with Cr and with V in dilute alloys, whose contents of the substitutional solute are 0.2 at.% Cr or 0.05 at.% V at the maximum, and reported that the interaction energy ΔE was –0.18 eV (N–Cr) and –0.21 eV (N–V) [31]. While continuing these investigations we have been attempting to evaluate ΔE from measurements of the solubility. In this section we present the results of recent experiments on N–Cr and C–Cr [32].

4.1. Experimental procedures

Five dilute Fe-Cr alloys were 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 of pure iron and the Fe–Cr alloys. To eliminate deformation textures possibly formed by the cold-work, the wires were annealed at 1223 K (above the α / γ transformation temperature) for 1 h in a vacuum. The wires were then subjected to annealing in a flowing wet hydrogen atmosphere of 1 atm at 973 K for 24 h. The wet hydrogen was provided by feeding a dry hydrogen gas through a bath of pure water maintained at 310 K. By this treatment the contents of C

and N were reduced to below a few at. ppm, which was verified by measuring the DC electrical resistivity and the Snoek relaxation of samples annealed at 973 K and quenched to 273 K.

Either nitrogen or carbon was introduced to the hydrogen-treated wires by placing them in a flow of a mixture of ammonia, or methane, and hydrogen [33, 34]. The total pressure was 1 atm and the flow rate was about 200 ml min^{-1}. The latter was electronically regulated within ± 1 ml min^{-1}. The activity of nitrogen or carbon was controlled by the proportions of the gas components and temperature. A typical setting was 2% ammonia and 98% hydrogen (in volume) at 823 K, 4% methane and 96% hydrogen at 973 K. The contents of N and C in the nitrided or carburized samples were determined by combustion analysis.

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.

4.2. Effect of Cr on the solubility of N

Wire samples of 0, 0.3, 0.6, and 0.9 at.% Cr were nitrided at 836 K for 11.5 h under three different levels of N activity, (1) 2.69×10^{-4}, (2) 3.96×10^{-4}, and (3) 5.13×10^{-4}. The proportion of hydrogen and ammonia was 990 : 10, 985 : 15, and 980 : 20, respectively. The nitriding time was chosen at twice the time required for the concentration of N at the centre of the wire reach 95% of that at the surface.

The N contents of the nitrided samples determined by combustion analyses are shown in Fig. 4. As they increase smoothly with the concentration of Cr in a fashion indicated by Eq. 2b and are all well below the solubility limit of N in unalloyed iron at 836 K (against the precipitation of Fe$_4$N), which is over 3,000 at. ppm [35], we assume that they represent the equilibrium solubility in the α single phase. According to the solubility product of Cr and N reported by Imai et al. [36], the solubility limit is reduced to about 800 at. ppm for 0.9 at. % Cr at 836 K. The uppermost value in Fig. 4 is close to this limit but is still lower than that. By applying Eq. 2b to each set of data, the interaction coefficient $\varepsilon_N^{(Cr)}$ is found to be in the range from –60 to –55. The same data are plotted in the form of Henry's law, $a_N = \gamma_N x_N$, in Fig. 5 (a). Each set of data for the same Cr concentration x_{Cr} follows the expected linear relation. The values of the activity coefficient γ_N are plotted against x_{Cr} in Fig. 5 (b). The slope in this diagram is the interaction coefficient $\varepsilon_N^{(Cr)}$, and is determined to be -58.5 ± 3.2 by linear regression. This is close to the values reported previously by Taneike [37] and Okamura [38], who carried out essentially the same experiments, but the range of uncertainties turns out significantly smaller in the present work, which is due mostly to the higher concentrations of Cr employed here.
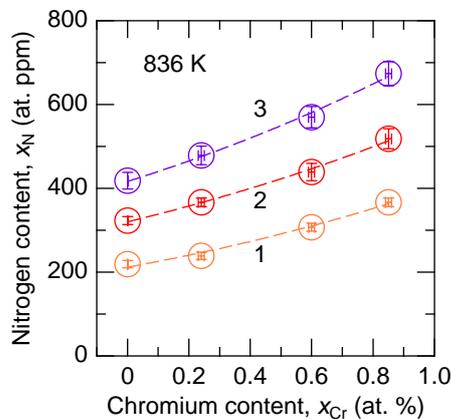

Fig. 4   N contents in pure iron and dilute Fe–Cr alloys nitrided at 836 K under three different levels of N activity (see text). The dashed curves are drawn by fitting Eq. 2b to each set of data.
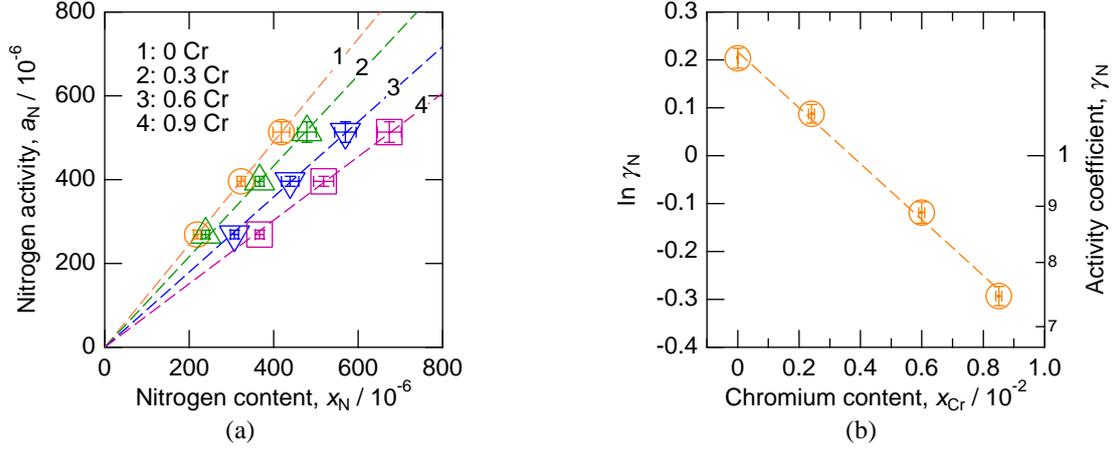
Fig. 5　(a) The same data as Fig. 4 plotted in the form of Henry's law, and (b) the activity coefficient of N as a function of Cr concentration.

The interaction energy is obtained from the interaction coefficient by inverting Eq. 4,

$$\Delta E = -kT \ln\left(1 - \frac{m}{z}\varepsilon_i^{(j)}\right). \tag{7}$$

While the parameter m is 3 for interstitial solute atoms occupying octahedral sites in the bcc structure, the number of equivalent trap sites per substitutional solute atom, z, depends on the details of interaction. It is, for example, 6, 12, or 18 if the trap sites are the first nearest neighbour sites, the second nearest neighbour sites, or both. The values of ΔE derived for the three cases from the interaction coefficient given above are listed in Table 1, together with those determined by Guan et al. [31] from the Snoek relaxation. The two sets of evaluations agree only for the third, where both the first and second nearest neighbour sites are assumed to be trap sites of similar importance.

Table 1　Interaction energy ΔE between N and Cr in α iron evaluated from the solubility [this work] and from the Snoek relaxation [31].

Trap sites*	ΔE / eV	
	From solubility at 836 K	From Snoek relaxation at 300 K
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.

4.3. Effect of Cr on solubility of C

Alloys containing 0, 0.6, 1.2, and 1.8 at.% Cr were used for studying the interaction between C and Cr. Wire samples 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 with a volume ratio of 197 : 3.1 and 173 : 9.1, respectively. The Cr concentrations of the alloys are twice as high as those for nitriding, since a previous investigation [38] suggested weaker influence of Cr on C on N.

The C contents determined by combustion analyses are shown in Fig. 6. In contrast to the case of N (Fig. 4), the solute Cr has virtually no effect on the solubility of C. As the temperature of carburization was higher than the temperature of nitriding, which was to avoid exceeding the much lower solubility limit of C than that of N, detecting effects on the solubility is even more difficult, but the small

error bars demonstrate that the interaction coefficient $\varepsilon_C^{(Cr)}$ is very small in magnitude at this temperature. Fitting Eq. 2b to the data sets 1 and 2 gives –4 and +2, respectively, to $\varepsilon_C^{(Cr)}$. If the interaction is attractive, the absolute magnitude of the interaction energy ΔE must be less than 0.1 eV.
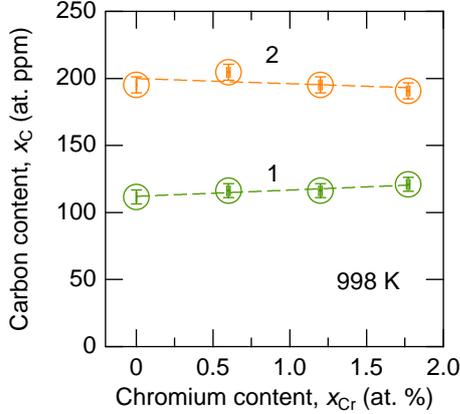

Fig. 6   Concentrations of C in pure iron and dilute Fe–Cr alloys carburized at 998 K under two different levels of carbon potential.

4.4. 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 in a vacuum and were quenched to 273 K. The mechanical loss of the supersaturated solid-solution samples was measured by the free-decay method at resonance frequencies around 1 Hz as a function of temperature from 150 K to 400 K by heating or cooling at a rate of 1 K min^{-1}.

Figure 7 shows the results of the measurements for samples containing about 110 at. ppm C. Unlike the case of Fe–Cr-N alloys [30, 31], 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. These results are in agreement with the previous study [38] 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 presented above. Saitoh et al. 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 [39]. We suspect that solute atom clusters were developed in their samples, as they were prepared by decarburization from materials containing larger amounts of C through extended heat treatments. It is possible that the higher concentration of C promoted formation of Cr–C atom clusters.
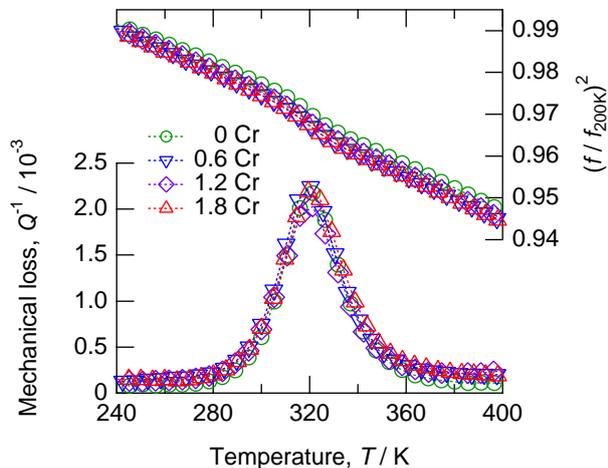

Fig. 7   The mechanical loss Q^{-1} (lower) and the square of the resonance frequency f of carburized samples containing 110 to 120 at. ppm C. The frequency is normalized to the value at 200 K.

4.5. Comparison with previous reports

Wada [40] carried out similar carburizing experiments on a series of Fe–Cr alloys up to 8.7 at. % Cr at 985 K and obtained –72 ± 2 as the interaction coefficient. Nishizawa et al. [41] 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 the 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 concentrations in each section of the annealed multiple, they obtained negative values for the interaction coefficient, indicating attractive interaction, corresponding to ΔE of about –0.2 eV[1]. These data in the literature suggest much stronger attractive interaction between C and Cr than in the present work. One of the possible origins of this discrepancy is clustering of Cr atoms driven by the presence of C atoms; isolated Cr solutes may not trap a C atom but small solute-atom clusters consisting of a certain number of Cr and C atoms may be favoured in energy. Such clusters must stabilize themselves further as they grow and eventually form alloy carbides.

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 [32]. It is a gradual, or stepwise transition from a paraequilibrium state (in which the distribution of the slowly diffusing substitutional solute atoms is frozen) to the true equilibrium state. The transition is to proceed significantly if the annealing time is sufficiently 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, more than 100 h, than in the present experiment. A variety of metastable solute-atom clusters may appear during the transition. The effective interaction energy for those transient states would vary depending on the structure and size of the clusters. To determine the interaction energy between single interstitial and substitutional 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.

5. SUMMARY AND PERSPECTIVE

Attractive interaction between the interstitial and substitutional solute atoms can be studied by precisely measuring the influence of the latter on the equilibrium solubility and the elementary diffusional jumps of the former, from which the interaction energy ΔE can be evaluated. Recent experiments on the interaction of N and Cr gave consistent results, $\Delta E \approx$ –0.17 eV, a quantitative indication of attractive interaction between isolated solute atoms, or a trend of close-pair formation. In contrast, the results on C–Cr suggest much weaker interaction if attractive, or it could be even repulsive. 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 verify 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.

In parallel with the need for investigating the structure, stability and formation kinetics of various solute atom clusters, much work has to be done on the elementary cluster, an i–s solute atom pair. As suggested by Table 1 the geometrical configuration of a close pair is critical in interpreting the macroscopic measure of the interaction. In the analysis of the Snoek relaxation the potential energy profile that reproduces the observation is not unique; there are several energy landscapes that gives the observed relaxation spectrum equally satisfactorily. There is a possibility of determining the real trap site from the point symmetry of the i–s pair, by measuring the anelastic relaxation using single crystal samples. Theoretical approaches such as ab initio calculations of electronic structures must be useful in this particular problem, but are to be employed more extensively to better understand the nature of the solute–solute interaction. There are still a number of important alloying elements that are to be studied.

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[1] Their data are those shown in Fig. 2 of this article.

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