1. Introduction

Effects of alloying elements on the microstructure and properties of steels often occur indirectly through their influence on the behaviour of carbon and nitrogen. One of the origins of such effects is the interaction between the interstitial and substitutional (i–s) solute atoms \[1, 2, 3\]. Detailed and quantitative knowledge of the i–s interaction is one of the key elements in predictive material design, which is needed for high-performance and/or highly durable steels with efficient use of material resources. From this viewpoint the Snoek relaxation in dilute ternary iron alloys \[4, 5, 6\] attracts renewed interest, as it serves as a unique tool for probing the local interaction between the solute atoms \[7, 8, 9\].

Changes in the solubility and diffusivity of the light interstitial solutes are understood as originating from their trapping into low-energy sites in the vicinity of a substitutional solute atom, as illustrated in Fig. 1. If the nearby sites are energetically unfavourable, on the other hand, blocking occurs. How the distribution and diffusion rates of the interstitial solute atoms are affected is governed by the interaction energy \(\Delta E\) (defined negative for attraction, and positive for repulsion), and it is what one wishes to determine. For hydrogen in metals, theories of trapping by various defects, including dislocations, vacancies, and solute atoms, have been developed, and experimental studies have been performed extensively since 1970s \[10\]. Concerning C and N in iron, there are a fairly large number of reports on the effects of alloying elements on the equilibrium solubility in liquid iron and \(\gamma\) iron, and in the latter the effects on the diffusivity of C have also been analysed. On the other hand, for \(\alpha\) iron very few experimental data are available in the first place, even though knowledge concerning the \(\alpha\) phase is most desired as a scientific basis for advanced ferritic steels. This lack of information is primarily due to the very limited solubility C and N in the bcc phase, which makes precise experiments and analyses difficult.

The group of the present author has been working on the problem, aiming at accurately determining the i–s interaction energy for a series of substitutional solute species, on the basis of the established experimental techniques and methods of analysis \[8\]. It is a need from the steel industry \[9\], and is growing to one of the societal demands from the viewpoint of ‘element strategy’ \[13\]. With the purpose of introducing this activity and also attracting more attention to the subject, this article presents the models, established facts, and recent developments of experimental and theoretical studies.

**SOLUTE–SOLUTE INTERACTION IN \(\alpha\) IRON: THE STATUS QUO**

**WZAJEMNE ODDZIAŁYWANIE ATOMÓW SUBSTYTUCYJNYCH I MIĘDZYWĘZŁOWYCH W ŻELAZIE ALFA: STATUS QUO**

Abstract. An overview is presented on the interaction of substitutional solutes with carbon and nitrogen in \(\alpha\) iron, which is an important factor in controlling the properties of steels. Starting from a simple model of trapping of the interstitial solute atoms by substitutional solute atoms, the principles of experimental methods for quantitative studies are described, focussing on the Snoek relaxation and solubility measurements, and the knowledge acquired by such experiments is reviewed. An account of recent theoretical approaches to the interaction is also given.

**Keywords** iron and steel, carbon, nitrogen, solubility, diffusion, trapping, Snoek relaxation

Przedstawiono przegląd oddziaływań atomów substytucyjnych z atomami węgla i azotu w żelazie alfa, które jest ważnym czynnikiem wpływającym na właściwości stali. Zaczynając od prostego modelu pułapkowania rozpuszczonych atomów międzywęzłowych przez atomy substytucyjne, przedstawione są zasady metod eksperymentalnych stosowanych w badaniach ilościowych, koncentrując się głównie na badaniach relaksacji Snoeka i pomiarach rozpuszczalności. Przedstawiono przegląd wiedzy nabytej w takich eksperymentach oraz najnowszej próby teoretycznego opisu ww oddziaływań.

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The effect of the micro-alloying elements, which are transition metal species located in the periodic table on the left of iron, on N are similar to that found in Fe–V–N, and other transition metal species located in the periodic table on the right of iron, on N are also similar to that found in Fe–V–N. The effects depend on the details of the interaction, and are, for example, 6, 12, or 18, if the trap sites are the first nearest neighbour sites of the substitutional solute atom, the second nearest neighbour sites, or both the two types of sites, respectively.7

With this simple two-level trapping model, the fraction of trapped interstitial solute atoms is given by

\[ f_{\text{mp}} = \frac{x_i \frac{z}{m} \exp \left( -\frac{\Delta E}{kT} \right)}{1 - x_i \frac{z}{m} \left[ 1 - \exp \left( -\frac{\Delta E}{kT} \right) \right]}. \]  

The effect of the interaction on the diffusion of the interstitial solute atoms is described as

\[ D_i = \frac{D_i^0}{1 - x_j \frac{z}{m} \left[ 1 - \exp \left( -\frac{\Delta E}{kT} \right) \right]} \]  

for the same two-level model with an additional assumption that the solubility of the interstitial solute species is unchanged. Here, \( D_i \) and \( D_i^0 \) are the diffusion coefficients of the interstitial solute atoms with and without the substitutional solute atoms, respectively. Equation (3) shows that the diffusivity is lowered by the same factor as the solubility is increased in Eq. (1). If the binding is stronger than with a vacancy or an edge dislocation (which are believed to be 0.5 to 0.7 eV), trapping by substitutional solute atoms can be significant since the density of the trapping centres can be of the order of \( 10^{-3} \) to \( 10^{-2} \), which almost never occurs for intrinsic point defects or dislocations.

It is to be noted that studying such trapping effects is not easy in practice for C/N in α iron because of the limited solubility of the interstitial solutes. The concentrations are at most of the order of \( 10^{-3} \), and one needs to detect small variations induced by the substitutional solutes. It is further difficult for substitutional solute species that form stable alloy carbides and/or nitrides, since the composition range of the ternary solid solution is prohibitively narrow for any evaluation of solubilities or diffusivities to be made at reasonable accuracy.

3. Effect on the Snoek relaxation

It was discovered around 1950 that the Snoek relaxation of N in iron was strongly affected by small addition of alloying elements, and since then a number of similar observations have been reported [4-6, 16]. The effects are diverse, depending on the solute species: while in some cases new components appear and the relaxation profile becomes complex, in other cases the Snoek peak is only broadened and lowered. The case of Fe–V–N alloys [17, 18], in which a well-defined new peak appears at a higher temperature than the ordinary peak, is a simple example of the former, whereas for C the latter is almost always the case [6, 19].

The effects of the micro-alloying elements, which are transition metal species located in the periodic table on the left of iron, on N are similar to that found in Fe–V–N, and can be understood in terms of trapping: with increasing the trap site density the ordinary Snoek relaxation is decreased in magnitude and an additional relaxation component is produced, whose relaxation rate is lower because of the higher activation energy for the jump out of the trap site. On the basis of the foundation laid by Meijering [20], theories for the kinetics and thermodynamics of the complex relaxation are well established [21, 22, 23], and those observations mentioned above can be analyised to evaluate the interaction energy by comparing theoretical relaxation profiles expected from assumed site energy distributions with experiment [8]. On the other hand, the effects of the same substitutional species, which are naively expected to interact with C similarly to N, on the Snoek relaxation of C are primarily to decrease the relaxation magnitude, only slightly distorting the profile [19]. Analysing such profiles by the same method is not impossible [24], but

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Fig. 1. Schematic illustration of the potential energy profile for an interstitial solute atom (small filled circle) in the vicinity of a substitutional solute atom (large filled circle) in a bcc crystal.
it involves much ambiguity and, therefore, one cannot derive a unique conclusion.

We turn now to some recent results on Fe–Cr–C and Fe–Cr–N alloys. The observation by Saitoh et al. [19] that the relaxation strength is reduced by the addition of Cr seems to indicate that Cr and C do interact with each other, even though no quantitative evaluation can be made. The interaction between Cr and C is expected to be attractive, as they form stable carbides in iron, and was in fact reported to be so from the equilibrium solubility of C in dilute Fe–Cr alloys [25, 26]. However, the latest experiment by the group of the present author does not indicate any interaction. Figure 2 shows the profiles of Snoek relaxation of a set of dilute Fe–Cr alloys carburized together in a mixture of methane and hydrogen at 998 K ($Q^{-1}$: mechanical loss, i.e., internal friction, $G$: shear modulus, $G_u$: unrelaxed value of $G$). The concentrations of C, which were determined by combustion analysis, are $116 \pm 10$ mol ppm throughout. The samples were solution-treated at the carburized temperature, and mechanical loss was measured using an inverted torsion pendulum instrument by the free decay method at frequencies around 1 Hz. From the amounts of C absorbed and the Snoek relaxation profiles, Cr and C atoms in the (supersaturated) bcc solid solution appear to have virtually no interaction. A possible explanation of this discrepancy is that in the experiments of the earlier reports [25, 26] the materials did not stay in the bcc single phase. In our experiments the carburizing time was 4.5 h, which was chosen to be as short as possible to minimize diffusion of Cr while still allowing C atoms to distribute almost uniformly in the wire sample of 1 mm in diameter. The diffusion distances of C and Cr during the carburizing, at 998 K for 4.5 h, are about 1 mm and 0.5 μm, respectively, and the latter is some $10^2$ to $10^3$ times the average separation between Cr atoms in the original solid-solution with the Cr concentration of 0.6 mol %, for example. In contrast, the equilibration time in the work of Wada [25] was more than 100 h at 985 K, and that in the work of Nishizawa et al. [26] was over 2400 h at 973 K or 1073 K. Judging from the concentrations of Cr and C in their experiments, precipitation of chromium carbides, probably Cr$_7$C$_3$, or at least clustering of Cr and C atoms, must already have occurred in some of the samples. The present experiment must have more nearly maintained the original distribution of the substitutional solutes in the solid solution even in samples in which the concentrations of the two solute species exceed the solubility limit (the solubility product of the carbide phase), and, therefore, allows the study of the interaction between single Cr and single C atoms dissolved in the bcc matrix.

Figure 3 shows the Snoek relaxation profiles in a set of Fe–Cr alloys nitrided in a mixture of ammonia and hydrogen at 863 K for 8.5 h. Unlike the previous case for C, the amounts of N absorbed are larger in the samples of higher Cr contents, from 140 to 270 (± 10) mol ppm, indicating attractive interaction of Cr with N. It is to be noted that because the solubility product of Cr and N at this temperature is so small that in all but the unalloyed iron precipitation of CrN must have occurred during nitriding, if kept for a sufficiently long time. The measurements were made under supersaturated para-equilibrium condition, and turned out markedly different from each other; the influence of Cr on the diffusion of N is also strong, again unlike the case of C. In a previous report [8] the effect of Cr was investigated at Cr concentrations below 0.2 mol % to observe gradual increase of the strength of the extra relaxation component, which is assumed to be due to N atoms trapped to a Cr atom. The results reported in the previous paper were those of isothermal frequency-sweep measurements, and the extra component observed there appears in the present temperature-sweep experiment at 325 K. Here, at and above 0.24 % Cr, this component no longer increases in magnitude but decreases with Cr content, and instead yet another new component begins to grow at the low temperature side of the standard Snoek peak (which is already absent at 0.24 % Cr). This low-temperature relaxation may be attributed to N atoms jumping in the vicinity of close pairs of Cr atoms, which might have formed during nitriding; agglomeration of Cr and N atoms is likely to occur, as Cr forms stable alloy nitrides.

Fig. 2. Snoek relaxation of Fe–Cr alloys carburized and solution-treated at 998 K. Numbers in the legend are Cr contents in mol %.

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1 A preliminary report was made in conference proceedings in 2012 [9].
From the two experimental results shown above, it is evident that attention should be paid to experimental conditions for solute atoms whose solubilities in the primary solid solution phase are limited; atomic interaction between such solute atoms can be studied only under para-equilibrium conditions, which can be attained by considering the kinetics in possible redistribution of the solute atoms. In view of these examples, it now seems necessary to re-examine many of the results reported in the literature, at least to inquire under which conditions the experiments were made.

4. Effects on the equilibrium solid solubility

As mentioned in the Introduction, how the solubilities of C and N are affected by other elements in iron is important for its own sake in steelmaking, so that effects of tertiary elements on the equilibrium solubilities of C and N were investigated extensively for liquid iron, and also for γ iron. The data accumulated by the early 1970s were compiled by Fromm and Gebhardt [12]. Experimental results were analysed in terms of the interaction coefficient introduced by Wagner [11]. In his formalism, the effect of element \( j \) on the activity coefficient of component \( i \), \( \gamma_i \), is written as

\[
\ln \gamma_i = \ln \gamma_i^* + \varepsilon_{ij}^{(1)} x_j + ... \tag{4}
\]

where \( \gamma_i^* \) is the activity coefficient in the absence of \( j \), and

\[
\varepsilon_{ij}^{(1)} = \left( \frac{\partial \ln \gamma_i}{\partial x_j} \right)_{x_i,x_j \to 0} \tag{5}
\]

is the interaction coefficient between \( i \) and \( j \). If the two solute species interact attractively the activity coefficient of \( i \) is lowered, and the interaction coefficient is negative. The reverse is true if they interact repulsively.

If one wishes to evaluate the interaction coefficient by following this definition, one would prepare dilute alloys of different contents of component \( j \), and for each \( x_j \) determine the activity coefficient of \( i \), \( \gamma_i \), from the experimentally obtained relation between the activity and the concentration, \( a_i = \gamma_i x_i \), in the dilute limit of \( i \). The set of values of \( \gamma_i \) is then used to determine \( \varepsilon_{ij}^{(1)} \) by extrapolating \( x_j \) to zero. Alternatively one may equilibrate a set of the dilute alloys in an environment of a defined activity of component \( i \), measure the equilibrium concentrations of \( i \) in the alloys, and determine \( \varepsilon_{ij}^{(0)} \) in reference to the expression

\[
\ln x_i = \ln x_i^* - \varepsilon_{ij}^{(1)} x_j + ... \tag{6}
\]

which is derived from Eq. (4) using the relation \( a_i = \gamma_i x_i \). This procedure is simpler than the first, but should be made at sufficiently low concentrations of \( i \) to guarantee the condition \( x_i \to 0 \). It is not, therefore, necessarily easier.

The interaction coefficient of selected substitutional solute elements with C and that with N in γ iron, based on the estimates by Nishizawa [27], are shown in Figs. 4 (a) and 4 (b). A systematic trend is seen in both: the interaction is more attractive for elements located on the left of Fe in the periodic table, while it is weakly repulsive for those on the right. The corresponding data for α iron, mostly from the ongoing experimental studies of the group of the present author, are shown in Figs. 5 (a) and 5 (b). The general trend for N is similar to what is observed in γ iron, but the data for C with the transition metal elements do not appear to be systematic. As discussed in the previous section, C–Cr interaction is negligibly weak, while N–Cr is significantly attractive, for example.

Those interaction coefficients can be interpreted in terms of the local interaction illustrated in Fig. 1. Again by the Fermi-Dirac statistics with the two-level trap model, it can be shown that the interaction coefficient is related to the interaction energy as follows [14].

\[
\varepsilon_{ij}^{(0)} = \frac{\varepsilon}{m} \left[ 1 - \exp \left( -\frac{\Delta E}{kT} \right) \right] \tag{7}
\]
In fact, Eq. (1) is derived by first rewriting Eq. (6) as

\[ x_i = x_i^0 \exp(-\varepsilon_i^0 x_j), \]

expanding it by assuming \(|\varepsilon_i^0 x_j| \ll 1\), and substituting Eq. (7) for \(\varepsilon_i^0\). This is a direct influence of component \(j\) on the solubility through the local interaction.

There can be, in addition, indirect influences of the tertiary component through some global changes of the solvent. One such change is the elastic distortion of the host crystal, as discussed by Sluiter [28]. When a solute species \(j\) is added the volume is either increased or decreased, and this leads to changes in the solubility of solute species \(i\). This effect can be important for interstitial solute species, as they induce a large volume expansion of the host crystal and, therefore, the solubility is sensitive to variations in the volume. In terms of the heat of solution \(\Delta H_i\), which describes the temperature dependence of the solubility as \(x_i \propto \exp[-\Delta H_i / (kT)]\), the ratio of the solubilities with and without component \(j\) is written as

\[ \frac{x_i}{x_i^0} = \exp\left(-\frac{\Delta H_i - \Delta H_i^0}{kT}\right), \]

where the circle as a superscript indicates the absence of \(j\). Comparison of this expression with Eq. (6), with Taylor expansion of \(\Delta H_i\), gives

\[ \varepsilon_i^0 = \frac{1}{kT} \frac{\partial \Delta H_i}{\partial x_j} = \frac{1}{kT} \frac{\partial \Delta H_i}{\partial \Omega} \frac{\partial \Omega}{\partial x_j} = \frac{1}{kT} \frac{\partial \Delta H_i}{\partial a} \frac{\partial a}{\partial x_j}, \]

where \(\Omega\) is the atomic volume, and \(a\) is the lattice parameter. The last equality is for the case of solvent crystals of cubic symmetry, where the volume change can be replaced by the change in the lattice parameter \(a\). Sluiter [28] also gave theoretical estimates of \(\partial \Delta H_i/\partial a\) for C and N by first princi-
ples calculations, thereby enabling quantitative evaluation of the effect of a particular solute species from its influence on the lattice parameter.

The experimentally observed interaction coefficient is in general the sum of the two contributions, namely,

$$\epsilon_i^{(L)} = \epsilon_i^{(j,k)} + \epsilon_i^{(i,G)},$$

where the first and the second terms on the right hand side indicate the local and global effects, Eqs. (7) and (9), respectively. Taking Cr as an example, substitutional Cr atoms increase the lattice parameter of bcc iron, whose rate is described as $$(1/a_0)(\partial a/\partial x_{Cr}) = +1.43 \times 10^{-2}$$, where $a_0$ is the lattice parameter of unalloyed iron [29]. The effect of the lattice parameter on the heat of solution of C and N in bcc iron was shown by Sluiter [28] to be $$a_0(\Delta H_i/\partial a) = -37 \text{ eV}$$. These numbers give $$(\partial a/\partial x_{Cr}) = -0.53 \text{ eV}$$ for both C and N. The contribution of the global effect, $$\epsilon_i^{(i,G)} = (\partial \Delta H_i/\partial x_{Cr})/kT$$, is estimated to be, for example, −6.2 at 998 K ($kT = 0.086$ eV), and −7.4 at 836 K ($kT = 0.072$ eV). In experiment, on the other hand, the interaction coefficient of C–Cr was found to be virtually zero at 998 K, whereas that of N–Cr was −58.5 at 836 K [9]. The contribution of the local interaction can now be obtained by subtracting the global contribution from the experimental values: $$\epsilon_i^{(i,L)} = +6.2$$ at 998 K, and $$\epsilon_i^{(i,L)} = -51.1$$ at 836 K. The former shows that the local C–Cr interaction is weakly repulsive, which does not contradict the observed effect on the Snoek relaxation. The latter indicates, on the other hand, that Δ$E$ for a N–Cr pair is in the range between −0.25 eV and −0.17 eV (depending on the number of trap sites per substitutional solute atom). This agrees satisfactorily with the estimate from the Snoek relaxation, −0.16 to -0.18 eV [8]. These two cases are illustrated in Figs. 6 (a) and 6 (b). For the local N–Cr interaction the number of trap sites per Cr atom, $z$, is assumed to be 18 (both the first and second neighbour sites). For C–Cr, $\epsilon_i^{(i,L)} = +6.2$ means that, in reference to Eq. (7), 18 to 19 interstitial sites around a Cr atom are blocked even at 998 K. We assume that Δ$E$ is already much larger than $kT$ and expect $\epsilon_i^{(i,L)}$ remain unchanged at lower temperatures. The interaction coefficient vs temperature curve exhibits various patterns, depending on the signs and the magnitudes of the two contributions. Careful examination of experimentally observed curve must provide a clue for clarifying the interaction.

5. Theoretical approaches

First-principles calculations are an indispensable tool of materials science today, and are applied to various defect-related problems in iron and steel [30]. Several reports on the i–s solute atom interaction in bcc iron are found in the literature. One of the earliest attempts is by Kamminga et al. [31], who computed the local interaction energy of N with Ti, V, Cr, Ni, and Mo at various distances using the supercell method. They found that only a N–Ti pair at the second neighbour configuration was favourable, with the interaction energy of −0.22 eV, but all the other combinations were repulsive. As N–V and N–Cr interactions are certainly attractive in experiment, with appreciable interaction energy of about −0.2 eV, their calculations did not satisfactorily reproduce the reality. Sawada et al. [32] made similar calculations for C with 3d transition metal elements from Ti to Cu. In almost all cases the interaction is strongly repulsive when a C atom is at the first neighbour or the second neighbour site of the substitutional solute atom, and the repulsion decreases gradually with increasing the distance. While the interaction with Co, Ni, and Cu, which is repulsive as in liquid and γ phases, may be considered reasonable, the strong repulsion with the elements on the left of Fe was contrary to expectation, as were most of the results for N by Kamminga et al. [31]. In a detailed study on C–Si by Simonovic et al. [33] the interaction was strong repulsion at the first and second neighbour positions, weak attraction (Δ$E$ ~ −0.1 eV) at some of the farther positions. Si decreases the volume of iron and, through the effect on heat of solution of C, $\partial \Delta H_C/\partial x_{Si} ~ 1.0$ eV, contributes to the interaction coefficient, $\epsilon_i^{(i,G)} ~ +12$ at 1000 K, for example. This already accounts for the experimental values of the C–Si interaction coefficient, +11 to +12 in the temperature range from 1000 to

![Fig. 6. Interaction coefficient of Cr with C (a) and N (b) in α iron determined from the solubility measurements (Total), estimated from the indirect effect through the volume change (Global), and derived from their difference (Local)](image-url)
1400 K [26], thereby suggesting that the local interaction can be ignored. More detailed analysis is possible by considering a statistical distribution of C atoms over the variety of trap sites and blocked sites, which will be the subject of the next task.

Sluiter presented results of calculations on the interaction of C/N with Cr, Nb, and Si [28], and pointed out that for Nb, whose size misfit is particularly large (+6.1 %), the second neighbour site can be favourable for N with an appreciable interaction energy (~ ~0.1 eV) as a result of displacements of Fe atoms in the neighbourhood, but generally the close neighbour sites are almost always unfavourable, i.e., the interaction is strongly repulsive for close-pair configurations. At this moment the reason why these state-of-the art calculations disagree with experiment is unknown. Nevertheless, the interpretation of the interaction coefficient, a phenomenological parameter of thermochemistry, in terms of the local (direct) effect and global (indirect) effect is a step forward. Since any solute species more or less distorts the host crystal, the indirect effect always exists, and for some solute species the interaction may be governed almost solely by this effect, as Sluiter discussed [28]. He compared the strength of the experimentally observed C-solute interaction with the excess heat of solution of C caused by that substitutional solute species, and found a fairly good correlation. It seems to suggest that the interaction with those species are mostly indirect, arising through the volume change of the solvent. It also seems to hint that the elements which are further away from the correlation — Ti, V, Nb, and W — local interactions could be important. Another point to be clarified concerns the contrasting differences in the interaction of C with 3d transition metal elements between α iron and the other phases. One of the possible origins is the strong anisotropic distortion produced by C and N in the bcc phase, while the distortion must be nearly isotropic in the fcc phase. In supercell calculations, point defects (here the solute atoms) are interacting with their images, and to evaluate the effects of elastic strains the energies associated with those long-range elastic interactions must be corrected. Application of a recently proposed method for this correction [34], which is expected to ameliorate the situation, is now under way.

6. Summary

The effects of alloying elements on the Snoek relaxation are a classic in the history of internal friction in metals, but now the i–s solute interaction in iron attracts renewed interest and deserves systematic investigation. Evaluation of the interaction can be made by analysing the complex Snoek relaxation profiles caused by the addition of the substitutional solute species, but while it serves a useful tool for N, in some cases the effect on the relaxation profile is not strong enough, or almost null. The latter is the case of most substitutional species on the Snoek relaxation of C, the more important interstitial element in the steel industry. A complementary method is to measure the effect of the alloying element on the solid solubility of C or N. Physical pictures for interpreting the phenomenological interaction coefficient are now established, and analyses of experimental results on the basis of these interpretations are expected to provide quantitative information on the global and local interactions. Verifications by theoretical studies are desired but there are still a number of puzzling questions.

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