Thermodynamic factor in FeAl DO$_3$-phase interdiffusion from X-ray diffuse scattering

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Abstract

The *interdiffusion coefficient* for DO$_3$-phase of FeAl alloy is related via the modified Darken equation to the tracer diffusivities of the constituents. The thermodynamic factor Φ entering the Darken equation for interdiffusion coefficient is expressed in terms of the energy parameters which describe the ordering process in the binary alloy. Our calculations show the dependence of Φ on the long-range order parameters. These calculations are performed with the energy parameters extracted from the X-ray diffuse scattering data.

Keywords: Fe-Al alloys, interdiffusion, thermodynamic factor.

1   Introduction

Intermetallic compounds (intermetallics for short) have attracted considerable interest during recent decades because of fundamental as well as technological reasons [1]. The fundamental interest is mainly concerned with structural instabilities of the relatively simple lattices sometimes exibiting cubic symmetry for different concentrations in a wide temperature range. In Fe-Al system the structural instabilities manifest themselves in a series of phase transitions which may be of first- or second-order. Fe-Al alloys form one of the classical alloy systems of long-standing interest. It represents magnetic and structural phase transformations, which may be driven by the magnetic interactions as well as other factors, such as volume per atom, relaxation, ordering tendencies, etc.

The increasing interest in aluminides due to their technological importance has recently triggered studies on Fe-Al intermetallics [2, 3, 4, 5, 6]. Monte-Carlo study of Fe-Al system was carried out by Schmid and Binder in the framework of the Ising-Heisenberg model[7].

The energy parameters used in this work were extracted from the experimental data. In Ref. [8] the theoretical study of ordering in Fe-Al alloys based on a density-functional generalized perturbation method was performed. They found that ordering tendencies in Fe-Al system are strongly dependent on the underlying magnetic structure as well as the local magnetic moments. Ordering tendencies show a significant dependence on the alloy Wigner-Seitz radius. It is concluded that the concentration dependence of the pair interactions in the ferromagnetic model is significant.

Fe-Al alloy has a complicated phase diagram [9]. For equiatomic composition the paramagnetic disordered bcc phase (A2) transfers into paramagnetic B2-phase at the temperature 1068C. At the atomic fraction of iron equal to 0.75 the paramagnetic A2 phase undergoes at 612C a phase transition to the two-phase mixture, where the B2 paramagnetic phase coexists with the ferromagnetic A2-phase. Further, at 552C, this state changes into a DO_3 paramagnetic phase which is mixed with a small amount of ferromagnetic A2. After 510C the DO_3 phase becomes ferromagnetic. A study of phase competition of these phases in a wide concentration region demands the concentration dependent effective potentials of interatomic interactions. A problem also arises in the case when the homogeneity regions of the ordering phases are wide. The procedure described in Ref.[10] for the estimation of the parameters of the effective mixing potential may be realized for different phases with the stoichiometric composition. Taking into consideration, for example, only phases that are stable from the Lifshitz criterion[11] and writing down the formulaes, analogous to those represented for the B2 phase in the ground state, it is possible to evaluate the effective mixing potential for the different concentrations, corresponding to the stoichiometric compositions. The equilibrium between coexisting phases is described by the competition of the mixing energy term and the entropy of mixing. Typically the modelling of the mixing energy is carried out in terms of regular or subregular solid solutions. Parameters of these models are phenomenological constants, but in the common case they may be concentration-dependent. Such a dependence reflects the changes of the interatomic interaction of alloy constituents.

Self-diffusion can be studied in binary systems for which appropriate radioisotopes for both constituents of the alloy are available. With respect to the Fe-Al system suitable radioisotopes are available for Fe (e.g. ^{59}Fe) but not for Al[12]. In the framework of the Boltzmann-Matano method further insight to the diffusion behaviour of Fe-Al intermetallics can be gained from interdiffusion experiments. The *interdiffusion coefficient* is related via the modified Darken equation to the tracer diffusivities of the constituents. The thermodynamic factor Φ entering the Darken equation is proportional to the second derivative of the Gibbs free energy, G, of the alloy on the molar fraction of one of the components. These relations can be used to deduce the tracer diffusivity of Al provided that the tracer diffusivity of Fe, the interdiffusion coefficient and the thermodynamic factor are known. The mixing energy which enters G, could be calculated on the basis of the thermodynamical data received from the diffuse X-ray scattering measurements[13].

In the approach that we are suggesting in our paper the description of the temperature dependences of the long-range order parameter and of the free energy of ordering will be done according to the static concentration wave (SCW) theory[14]. The SCW method allows to take into account interatomic interactions at arbitrary distances. It establishes the relation between the statistical theory and the Landau-Lifshitz thermodynamic theory of second order transformations in alloy ordering. This method provides the possibility to predict a structure

of some ordered phase if pairwise interatomic interactions are estimated. Thus SCW theory overcomes several principal difficulties of the traditional theories of ordering[15, 16].

2   Study of the energy parameters for Fe-Al alloy

2.1   Concentration wave approach

The Gibbs free energy of Fe-Al alloy, G, may be written in the form

$$G = c_{Fe}G_{Fe} + c_{Al}G_{Al} + \Delta G(c_{Fe}, c_{Al}), \tag{1}$$

where ΔG is the Gibbs free energy of mixing, G_{Fe} and G_{Al} are Gibbs energies of Fe and Al, respectively. Atomic fractions of Fe and Al are written by c_{Fe} and c_{Al}. ΔG depends nonlineary on fractions of alloy components and contains the enthalpy of mixing ΔH and the excess entropy of mixing. For ambient pressure ΔH is practically identical to the internal energy of mixing ΔU.

Description of the temperature dependences of the long-range order parameter (LRO) and of the free energy of ordering may be done according to the SCW theory[14]. In the framework of the SCW theory the internal mixing energy of absolutely ordered phase U is written in terms of pairwise interactions

$$U = \frac{1}{2}V(0)c_{Fe}^2 + \frac{1}{2}\sum_{s,j} \gamma_s^2 \eta_s^2 V(\vec{k}_s^{(j)}). \tag{2}$$

Summation in Eq.(2) is produced over the stars of vectors satisfying the Lifshitz criterion[11], s, and over the vectors of the star, j. η_s - are the long-range order parameters, that are describing the ordering in the superstructure, γ_s are the structural constants depending on the symmetry of the ordering phase. $V(\vec{k}_s)$ is the Fourier transform of the mixing potential $V(R) = V_{Fe-Fe}(R) + V_{Al-Al}(R) - 2V_{Fe-Al}(R)$ that is calculated in the superstructure reciprocal lattice vectors $\vec{k}_s$

$$V(\vec{k}_s) = \sum_{\vec{R}} V(\vec{R})e^{i\vec{k}_s\vec{R}}, \tag{3}$$

$V(0)$ is just the same as (3) but for $\vec{k}_s = 0$. Vectors $\vec{k}_s$ belong to the stars of vectors describing the superstructure. In the case of Fe$_3$Al-type (DO$_3$) superstructure the vectors $\vec{k}_s^{(j)}$ that are responsible for the formation of this phase from the disordered bcc solid solution are $\vec{k}_1^{(1)} = 2\pi/a(111)$, $\vec{k}_2^{(1)} = 2\pi/a(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and $\vec{k}_2^{(2)} = 2\pi/a(\frac{-1}{2}\frac{-1}{2}\frac{-1}{2})$. As shown in Ref.[14] $\gamma_1 = \frac{1}{4}$ and $\gamma_2 = \frac{1}{2}$ for this structure. The vectors $\vec{k}_s^{(j)}$ define the site occupation probabilities for the ordered phase that is stable regarding to the formation of the antiphase domains in an alloy.

It is obvious that this mixing energy in the ground state depends only on the interaction potential between atoms in such a binary phase. If such potential is known it is possible to calculate the temperature dependence of the long range order parameters using the equations of the Bragg-Williams (BW) type

$$ln\left[\frac{(1 - c_{Fe} + 1/4\eta_1 - 1/2\eta_2)(c_{Fe} - 1/4\eta_1 - 1/2\eta_2)}{(1 - c_{Fe} + 1/4\eta_1 + 1/2\eta_2)(c_{Fe} - 1/4\eta_1 + 1/2\eta_2)}\right] = \frac{V(\vec{k}_2)}{kT}\eta_2, \tag{4}$$

$$ln\left[\frac{(1 - c_{Fe} + 1/4\eta_1 + 1/2\eta_2)(c_{Fe} + 1/4\eta_1)}{(1 - c_{Fe} - 1/4\eta_1)(c_{Fe} - 1/4\eta_1 - 1/2\eta_2)}\right] = -\frac{V(\vec{k}_1)}{2kT}\eta_1 - \frac{V(\vec{k}_2)}{2kT}\eta_2$$

Here k is the Boltzman constant. Substituting $\eta(T)$ dependence into Eq.(2) one can immediately obtain the temperature dependence of the internal energy.

In the framework of the SCW theory the expression for the Gibbs free energy of mixing (neglecting the $p\Omega$ term) is

$$\begin{aligned}
\Delta G = & \frac{1}{2}V(0)c_{Fe}^2 + \frac{1}{32}V(\vec{k}_1)\eta_1^2 + \frac{1}{16}V(\vec{k}_2)\eta_2^2 + kT\{\frac{1}{2}[(c_{Fe} + \frac{1}{4}\eta_1) \cdot \\
& ln(c_{Fe} + \frac{1}{4}\eta_1) + (1 - c_{Fe} - \frac{1}{4}\eta_1)ln(1 - c_{Fe} - \frac{1}{4}\eta_1)] + \\
& \frac{1}{4}[(c_{Fe} - \frac{1}{4}\eta_1 - \frac{1}{2}\eta_2)ln(c_{Fe} - \frac{1}{4}\eta_1 - \frac{1}{2}\eta_2) + \\
& (1 - c_{Fe} + \frac{1}{4}\eta_1 + \frac{1}{2}\eta_2)ln(1 - c_{Fe} + \frac{1}{4}\eta_1 + \frac{1}{2}\eta_2) + (c_{Fe} - \frac{1}{4}\eta_1 + \frac{1}{2}\eta_2) \cdot \\
& ln(c_{Fe} - \frac{1}{4}\eta_1 + \frac{1}{2}\eta_2) + (1 - c_{Fe} + \frac{1}{4}\eta_1 - \frac{1}{2}\eta_2)ln(1 - c_{Fe} + \frac{1}{4}\eta_1 - \frac{1}{2}\eta_2)]\}.
\end{aligned}$$

The values of $V(0)$ and $V(k_s)$ may be obtained from diffuse X-ray scattering data as discussed in Ref.[13]. Values $V(0)/k = 5800\ K$, $V(\vec{k}_1) = -6400\ K$, and $V(\vec{k}_2) = -3700\ K$ are taken from the same paper. Results of calculations of the temperature dependence of the long range order parameters in DO_3 Fe-Al phase in the stoichiometric composition are presented in Fig. 1. Turning to Eqs.(4,5) with the same values $V(\vec{k}_s)$ we may study the temperature dependence of the thermodynamic factor.

2.2 Calculations of the thermodynamic factor

In an interdiffusion experiment diffusion couples are formed which initially consist of homogenous alloys of different compositions. The composition depth distribution which develops during a diffusion anneal is determined by electron microprobe analysis and evaluated using, e.g., the Boltzmann-Matano method. In this way interdiffusion coefficients $\tilde{D}$ are determined. The interdiffusion coefficient is related via the so-called modified Darken equation [17]

$$\tilde{D} = (D_{Fe}^* c_{Al} + D_{Al}^* c_{Fe})\Phi S$$

to the tracer diffusivities of the constituents. Here S is the vacancy wind factor introduced by Manning [18]. S is usually close to unity. The thermodynamic factor is related via

$$\Phi = \frac{(1 - c_{Fe})c_{Fe}}{RT}\frac{\partial^2 G}{\partial c_{Fe}^2}$$

to the Gibbs free energy of the alloy. G is equal to $U - TS + p\Omega$ at pressure p and at volume Ω. U is the mixing energy, and S is the entropy.

Using the expression (1) for the free energy G and Eq. (6) for the free energy of mixing are able to calculate Φ from Eq.(8). In any case using the representation (1) it is easy understand that only ΔG contributes the thermodynamic factor Φ. Thus Φ is temperature
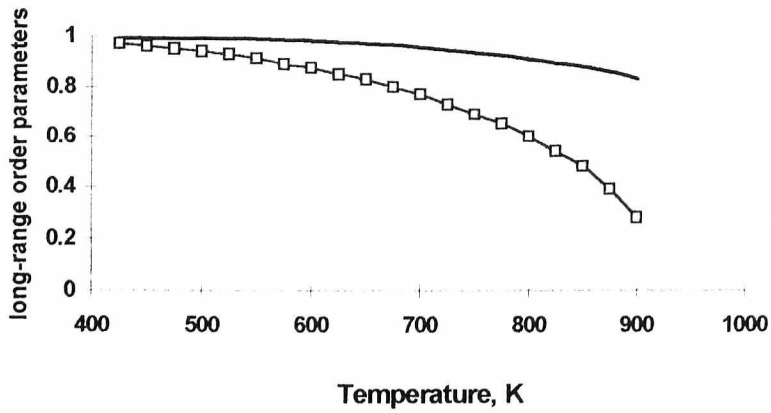
Figure 1: Temperature dependence of the long-range order parameters for Fe$_3$Al phase. The curve with markers is η_1 and the bold curve corresponds to η_2.
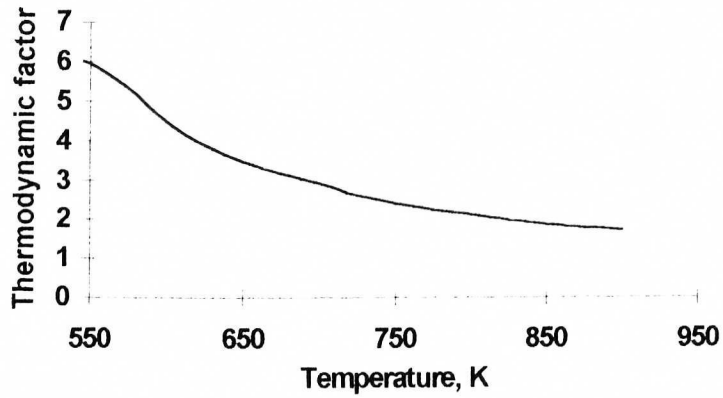

Figure 2: The thermodynamic factor Φ vs temperature for DO$_3$ Fe-Al phase.

and concentration-dependent and may be also a function of the state of order of phases studied.

In Fig. 2 we show the temperature dependence of Φ for stoichiometric composition of Fe_3Al DO_3 phase. With the growth of the temperature Φ decreases to $\Phi=1$. This value is approached at high temperatures. We may check the consistency of this result with the well-known data of behaviour of Φ for different systems. As it was discussed in [19] Φ is larger then unity for phases with negative deviations from ideality and smaller then unity in the opposite case. Negative deviations and condition $\Phi > 1$ are expected for systems with the tendency to order or with order[20]. Our result reflects the atractive interaction between constituents in DO_3 Fe-Al phase. We also obtained a good correspondence between our values and data calculated in Ref.[21].

3   Summary

We carry out calculations of the thermodynamic factor on the basis of the X-ray intensity measurements. Values of energy parameters are taken from Ref.[13]. The energy parameters obtained from the X-ray diffuse scattering experiments together with the statistical theory of the ordering allow to calculate the phase diagram with a very good accuracy. This means that thermodynamic functions of coexisting phases are also well defined as well as the phase competition at concentrantion and temperature changes. Results of calculations of the temperature dependence of the long-range order parameter in DO_3 Fe-Al phase are presented in Fig. 1. Substitution of these data into Eq. (6) and after that in (8) gives the values $\Phi(T)$, which are plotted in Fig. 2. The thermodynamic factor decreases with the increasing of the temperature. There is a reason for such a behaviour of the thermodynamic factor: *Increasing of the temperature leads to the decreasing of the long-range order parameter, which contributes in the behavior of* Φ.

Thus, the common features of the temperature dependence of the thermodynamic factor in DO_3-phase have been justified on the basis of the static concentration wave theory of ordering. The results of calculations of $\Phi(T)$ for FeAl DO_3-phase from the X-ray measurements data of the diffuse scattering may be useful for the determination of the tracer diffusivity of aluminium from the interdiffusion experiments.

Acknowledgements

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