Thermodynamic Factor Evaluated from Diffuse X-ray Scattering

Vlad Liubich*, Simon Dorfman**, David Fuks*
and Helmut Mehrer***

*Materials Engineering Department, Ben-Gurion University of the Negev, P.O.Box 653, 84105 Beer Sheva, Israel

**Department of Physics, Technion, 32000 Haifa, Israel

***Institut für Metallforschung, Universität Münster, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany

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

(Received August 31, 1998; In Final Form November 16, 1998)

Keywords: interdiffusion, binary alloys, ordering, thermodynamic factor, intermetallics

Intermetallic compounds or ordered alloys have recently attracted much attention as structural materials for high-temperature applications. Diffusion is ubiquitous at elevated temperatures and it is promoted by atomic defects. A knowledge of diffusion and of defect properties is therefore of great interest for the production of these materials and for their use in technological applications. The increasing interest in aluminides due to their technological importance has recently triggered studies on Fe–Al intermetallics using Mössbauer spectroscopy (MBS)⁽¹⁾. PAS^{(2)–(4)} studies provide information about the formation of thermal vacancies. Apart from wellknown geometric factors the self-diffusivity is the product of the thermal vacancy concentration times the mobility of the vacancies. A combination of both sets of experiments can be used to deduce the mobility of vacancies.

Few diffusion data on iron-aluminium alloys are available from the work of Larikov *et al.*⁽⁵⁾ (see also the data collection⁽⁶⁾). These data are limited to fairly high temperatures above 1173 K. This implies that for Fe-rich alloys diffusion has been studied in the disordered A2-structure only. Any influence of the state of order and of order-disorder transitions on the diffusion behaviour is unknown. Such information requires diffusion studies over much wider temperature ranges. Recently, data on diffusion of a Fe and an In-isotope in a wide temperature range have been published⁽⁷⁾.

It has been demonstrated that MBS can provide some insight into the atomic mechanism of Fe-atom diffusion in iron-aluminides⁽¹⁾⁽⁸⁾. However, MBS is not a routine method for diffusion studies. It is limited to a fairly narrow temperature window within which the jump time of Fe-atoms is comparable to the life time of the Mössbauer level of the Fe-isotope. MBS is neither able to provide information about Fe-diffusion over a wide temperature range nor can it provide any information about Al-diffu-

sion. This is why the experimental work on diffusion in Fe–Al has to be complemented by theoretical research.

Diffusivities in a homogeneous alloy can be determined with high accuracy using the radiotracer method. In binary systems for which appropriate radioisotopes for both constituents of the alloy are available comprehensive information about the diffusion behaviour can be obtained, if both tracer diffusivities are measured in alloys of various compositions as functions of temperature. With respect to the Fe–Al system appropriate and inexpensive radioisotopes are available for Fe component (*e.g.* ⁵⁹Fe) but not for Al. Further insight into the diffusion behaviour of Fe–Al intermetallics can also be gained from interdiffusion experiments. In an interdiffusion experiment diffusion couples are formed which initially consist of two homogeneous 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 eq. (9)

$$\tilde{D} = (D_A^* c_B + D_B^* c_A) \Phi S \quad (1)$$

to the tracer diffusivities D_i^* of the constituents. Here c_i denotes molar fractions, Φ the thermodynamic factor and S the vacancy wind factor introduced by Manning⁽¹⁰⁾. S is usually close to unity. The thermodynamic factor is related via

$$\Phi = \frac{c_A c_B}{RT} \frac{\partial^2 G}{\partial c_i^2} \quad (2)$$

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

It follows from eq. (2) that the thermodynamic factor may be expressed in terms of the coefficient of the thermodynamic activity, γ_i , of species i (A or B), which may be measured for different temperatures and concentrations in the homogeneity region of the intermetallic phase under consideration. Although the equation

$$\Phi = 1 + \frac{\partial \ln \gamma_i}{\partial \ln c_i} \quad (3)$$

shows the direct link of γ_i with the thermodynamic factor it seems to be a difficult and time-consuming procedure to perform measurements of γ_i for different concentrations and temperatures. This is usually done at some fixed temperature (see, for example, the work of Jacobson and Mehrotran⁽¹¹⁾). The obtained result is the function $\gamma_i = \gamma_i(c_i)$. If such a procedure is done for different temperatures the function Φ on concentration and temperatures would be obtained. The regions of definition of this function should be dictated by the needs of the interdiffusion experiments.

An alternative method of a direct study of the concentration and temperature dependence of the thermodynamic factor may be selected. This method is based on measurements of absolute intensities of X-ray scattering spectra of single crystals of disordered equilibrium alloys. These measurements give the opportunity to obtain the Fourier transforms of the interatomic mixing potentials. For the details of such measurements we refer to⁽¹²⁾. According to⁽¹³⁾ these Fourier transforms are the energetic parameters which completely determine the thermodynamics of the ordering alloys in a self-consistent field approximation. As was shown in⁽¹²⁾ the energetic parameters obtained from diffuse X-ray scattering experiments together with the statistical theory of ordering⁽¹³⁾ 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 concentration and temperature changes.

In this paper we present the results of calculations of the temperature and concentration dependences of the thermodynamic factor for interdiffusion in B2 Fe–Al alloy. This dependence comes not only from the definition of $\Phi(c, T)$ from eq. (2) but is also determined by the ordering of the system. It depends directly on the long-range order parameter which is temperature- and concentration-dependent.

The Gibbs free energy G may be written in the form

$$G = c_A G_A + c_B G_B + \Delta G(c_A, c_B), \quad (4)$$

where ΔG is the Gibbs free energy of mixing. This value depends nonlinearly on the molar fractions of components and may be presented by means of different models for solid solutions: regular solid solutions, subregular solid solutions, etc. ΔG 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 . In any case using the representation of eq. (4) it is easy to understand that only ΔG contributes the

thermodynamic factor Φ .

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 static concentration wave (SCW) theory⁽¹³⁾. The SCW method allows one to take into account interatomic interactions at arbitrary distances. It establishes the relation between the statistical theory and the Landau-Lifshitz thermodynamical theory of second-order phase transformations in the ordering of alloys. This method provides the possibility to predict the structure of the ordered phase if the pairwise interatomic interactions are estimated. Thus SCW theory overcomes several principal difficulties of the traditional theories of ordering⁽¹⁴⁾⁽¹⁵⁾.

We shall discuss here ordering only in the paramagnetic state because the temperature region of interest for the interdiffusion is far above the Curie temperature. Making use of the SCW theory the internal energy of mixing of ordered phase U may be written in terms of pairwise interactions in the following way

$$U = \frac{1}{2} V(0)c^2 + \frac{1}{2} \sum_s \gamma_s^2 \eta_s^2 V(k_s). \quad (5)$$

Here c is the concentration of the component A in the ordered phase, $V(k_s)$ is the Fourier transform of the mixing potential $V(R) = V_{AA}(R) + V_{BB}(R) - 2V_{AB}(R)$ that is calculated in the superstructure reciprocal lattice vectors k_s

$$V(k_s) = \sum_R V(R) e^{ik_s R}, \quad (6)$$

η_s are the long-range order parameters, that are describing the ordering in the superstructure, $V(0)$ is just the same as⁽⁶⁾ but for $k_s = 0$; γ_s are the structural constants depending on the symmetry of the ordering phase. Vectors k_s belong to the stars of vectors describing the superstructure. Summation in eq. (6) is performed over the stars of vectors satisfying the Lifshitz criterion⁽¹⁶⁾.

As an illustration of this technique we discuss the case of CsCl-type (B2) superstructure for Fe–Al alloy. In this case the vector k_s that is responsible for the formation of this phase from the disordered bcc solid solution is $k_s = 2\pi/a(111)$. As shown in Ref. (13) $\gamma_s = 1/2$ for this structure. The vector k_s defines the site occupation probabilities for the ordered phase that is stable with respect to the formation of antiphase domains in an alloy. The site occupation probability for Fe, $n(R)$, in the B2 FeAl superstructure is

$$n(R) = c + \frac{1}{2} \eta e^{2\pi i(x+y+z)}, \quad (7)$$

where x , y , and z are the coordinates of the bcc lattice sites and c is the atomic fraction of iron. At $c = 1/2$ and $\eta = 1$ this equation describes the completely ordered phase. With eq. (6) for this k_s it is easy to obtain

$$V(k_s) = -8V(R_1) + 6V(R_2) + 12V(R_3) - 24V(R_4) + 8V(R_5) \quad (8)$$

and

$$V(0) = 8V(R_1) + 6V(R_2) + 12V(R_3) + 24V(R_4) + 8V(R_5). \quad (9)$$

Here we restricted ourselves to five coordination shells of the Ising lattice denoted by R_i . Now we can get the expression for the energy of the stoichiometric composition of B2 phase in the form

$$U = \frac{3}{2} V(R_2) + 3V(R_3) + 2V(R_5). \quad (10)$$

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 this potential is known it is possible to calculate the temperature dependence of the long-range order-parameter using the equation of the Bragg-Williams (BW) type

$$\ln \left[\frac{\left(1 - c - \frac{1}{2}\eta\right) \left(c - \frac{1}{2}\eta\right)}{\left(1 - c + \frac{1}{2}\eta\right) \left(c + \frac{1}{2}\eta\right)} \right] = \frac{V(k_s)}{kT} \eta, \quad (11)$$

and the temperature of the order-disorder phase transition

$$T_c = - \frac{c(1-c)V(k_s)}{k}. \quad (12)$$

Here k is the Boltzman constant. Substituting $\eta(T)$ into eq. (5) one obtains the temperature dependence of the internal energy of mixing.

The expression for the Gibbs free energy of mixing ΔG (neglecting the $p\Omega$ term) is

$$\begin{aligned} \Delta G = & \frac{1}{2} V(0)c^2 + \frac{1}{8} V(k_s)\eta^2 + \frac{1}{2} kT \left[\left(c + \frac{1}{2}\eta\right) \ln \left(c + \frac{1}{2}\eta\right) \right. \\ & + \left(1 - c - \frac{1}{2}\eta\right) \ln \left(1 - c - \frac{1}{2}\eta\right) \\ & + \left(c - \frac{1}{2}\eta\right) \ln \left(c - \frac{1}{2}\eta\right) \\ & \left. + \left(1 - c + \frac{1}{2}\eta\right) \ln \left(1 - c + \frac{1}{2}\eta\right) \right]. \end{aligned} \quad (13)$$

Derivating ΔG twice with respect to concentration we obtain Φ as a function of concentration and temperature:

$$\Phi = \frac{c(1-c)}{kT} \Sigma_1 + c(1-c)\Sigma_2, \quad (14)$$

$$\begin{aligned} \Sigma_1 = & V(0) + 2c \frac{\partial V(0)}{\partial c} + \frac{c^2}{2} \frac{\partial^2 V(0)}{\partial c^2} + \frac{1}{8} \frac{\partial^2 V(k_s)}{\partial c^2} \eta^2 \\ & + \frac{1}{2} \frac{\partial V(k_s)}{\partial c} \frac{\partial \eta}{\partial c} \eta + \frac{1}{4} V(k_s) \left(\frac{\partial \eta}{\partial c} \right)^2, \\ \Sigma_2 = & \frac{1}{2} \left(\frac{\left(1 + \frac{1}{2} \frac{\partial \eta}{\partial c}\right)^2}{\left(c + \frac{1}{2}\eta\right) \left(1 - c - \frac{1}{2}\eta\right)} + \frac{\left(1 - \frac{1}{2} \frac{\partial \eta}{\partial c}\right)^2}{\left(c - \frac{1}{2}\eta\right) \left(1 - c + \frac{1}{2}\eta\right)} \right). \end{aligned}$$

Thus, Φ dependence on concentrations and temperature appears also because of concentration and temperature dependence of LRO parameter, $V(0)$, and $V(k_s)$ parameters. Values of $V(0)$ and $V(k_s)$ may be obtained from diffuse X-ray scattering data as discussed in Ref. (12).

We suggest in this paper the principal possibility for calculations of the thermodynamic factor on the basis of the X-ray intensity measurements. Values $V(0)/k = 5800$ K and $V(k_s)/k = -6400$ K were taken from Ref. (12), where they are concentration independent. Results of calculations of the temperature dependence of the long-range order parameter for different concentrations of iron in B2 Fe-Al phase are presented in Fig. 1. Substitution of these data into eq. (14) gives the values $\Phi(c, T)$, which are plotted in Figs. 2(a) and (b). The thermodynamic factor decreases with the increasing of the temperature (see Fig. 2). Φ at each temperature has the maximum value at the stoichiometric composition c_{st} and decreases symmetrically when the composition is deviated from c_{st} . There are two formal reasons for such a behaviour of the thermodynamic factor:

1. The maximum value of the long-range order parameter is defined from the conditions $\eta_{max} = 2c$ if $c \leq c_{st}$ and $\eta_{max} = 2(1-c)$ if $c \geq c_{st}$. At stoichiometric composition $c_{st} = 0.5$ for B2 phase $\eta_{max} = 1$, while at other compositions in this phase we obtain the same value η_{max} for symmetric deviations in composition. For example $\eta_{max} = 0.8$ for $c = 0.4$ and $c = 0.6$. This corresponds to the concentration disordering of the B2 phase. Note that η_{max} is independent on $V(k_s)$.

2. As follows from the results of diffuse X-ray scattering measurements (see Ref. (12)) $V(k_s)$ and $V(0)$ are independent on iron/aluminium concentration for Fe-Al alloy. This leads to the fact that $\eta(T)$ dependences are just the same for the symmetrical changes of composition from the stoichiometric one for B2-phase.

Assuming the absence of concentration dependences of $V(0)$ and $V(k_s)$ we will obtain Σ_2 in eq. (14) absolutely symmetric with respect to $c_{st} = 0.5$. Σ_1 is also symmetric in this case with respect to $c_{st} = 0.5$. It is worth to note that the concentration dependence of the thermodynamic factor may be nonsymmetric if $V(0)$ and $V(k_s)$ become functions of concentrations of constituents in an alloy. Some more common features of changes of Φ for B2-phase may be obtained from the analysis of eq. (14). It is easy to see that in the high-temperature limit, which corresponds to the disordered phase, the first term in eq. (14) is negligibly small, while the second one approaches unity. Thus $\Phi \rightarrow 1$ at this condition. With the concentrational disordering in B2-phase Φ decreases and at (a) $c \rightarrow 0$ or (b) $c \rightarrow 1$ the first term in eq. (14) seeks to zero, while the second one approaches unity for both (a) and (b) conditions. In this case $\Phi \rightarrow 1$. Our results show the decrease of the thermodynamic factor with increasing of atomic fraction of iron. This dependence has the same character as in the measurements of Ref. (11). The measurements were performed up to the atomic fraction of aluminium equal to 0.5. In the review⁽¹⁷⁾ the activity data of Radcliffe

Fig. 1 Results of calculations of the temperature dependence of the long-range order parameter for different concentrations of iron in B2 phase of Fe-Al alloy.

Fig. 2 The thermodynamic factor Φ for different temperatures and concentrations of iron for B2-phase of Fe-Al alloy. (a) T equal to 1173 K, and (b) T equal to 1373 K. Squares and the bold line correspond to the values of Φ with the partial derivative on concentration and triangles and the thin line correspond to the Φ values without this derivative.

et al.⁽¹⁸⁾ were discussed and compared with results of the other measurements. It was shown that all these data are in satisfactory agreement with each other. The thermodynamic factor obtained on the basis of the measure-

ments of Radcliffe *et al.* and Jacobson *et al.*⁽¹¹⁾ was calculated in Ref. (19). Comparison of different calculated data could be provided only at the fixed temperature and concentration ranges. The authors of Ref. (19) showed the disagreement between these data because they were obtained at different temperatures for the same concentration range. Unfortunately we are familiar only with the few data on diffuse X-ray measurements (see Ref. (12)). These measurements were performed for the different concentration range and any comparison with the data on activity measurements could be only qualitative. The quality of X-ray measurements used in our calculations were justified by the calculation of Fe-Al phase diagram, which was in a good agreement with experiment⁽¹²⁾.

We have shown in our paper the common features of the concentration and temperature dependences of the thermodynamic factor for B2-phase on the basis of the static concentration wave theory of ordering and calculated the function $\Phi(c, T)$ for FeAl B2-phase from the X-ray measurements data of the diffuse scattering. These results may be useful for the determination of the tracer diffusivity of aluminium from the interdiffusion experiments. In B2 intermetallic compounds, usually, anti-site atoms and/or point defects (vacancies) are present and they are very important to discuss characteristics of intermetallic compounds⁽¹⁷⁾. In our approach influence of defects is accounted by the use of the potential parameters $V(0)$ and $V(k_s)$ which are extracted from the experiment. Thus, we explore the potentials effectively considering the structure of the real alloy. Such advantages are typical features of semiempirical or empirical theories and allow to apply them very extensive.

Acknowledgements

This research was supported by a grant 418-038.10/95 from the German-Israel Binational Science Foundation (GIF) and by the special program of the Israel Ministry of Absorption. We are grateful to Dipl.-Phys. M. Eggersmann for comments on the manuscript.

REFERENCES

- (1) R. Feldwisch, B. Sepiol and G. Vogl: *Acta metall. mater.*, **43** (1995), 2033.
- (2) H.-E. Schaefer, R. Würschum, M. Sob, T. Zak, W. Z. Yu, W. Eckert and F. Banhart: *Phys. Rev. B*, **41** (1990), 11869.
- (3) H.-E. Schaefer and K. Badura-Gergen: *Defect and Diffusion Forum*, **143-147** (1997), 193.
- (4) J. Wolff, M. Franz, A. Broska and Th. Hehenkamp: *Defect and Diffusion Forum*, **143-147** (1997), 239.
- (5) L. N. Larikov, V. V. Geichenko and V. M. Fal'chenko: *Diffusion Processes in Ordered Alloys*, Naukova Dumka Publ., Kiev 1975, Nat. Bur. Stand. New Delhi: Amerind. Publi. Co., (1981), 176.
- (6) H. Mehrer, (ed.): *Diffusion in Solid Metals and Alloys*, vol. 26 of *Landolt-Börnstein, New Series*, Springer Verlag, (1990).
- (7) H. Mehrer, M. Eggersmann, A. Gude, M. Salamon and B. Sepiol: *Proceedings of the 4th International Conference on High-Temperature Intermetallics*, San-Diego, (1997), *Materials Science and Engineering A259-260* (1997), 889.
- (8) M. Eggersmann, B. Sepiol, G. Vogl and H. Mehrer: *Defect and Diffusion Forum*, **143-147** (1997), 339.
- (9) J. Philibert: *Atom Movements—Diffusion and Mass Transport in Solids*, Les Editions de Physique, (1991), 577.

- (10) J. R. Manning: *Diffusion kinetics of atoms in crystals*, van Norstrand, (1968), 257.
- (11) N. S. Jacobson and G. M. Mehrotran: *Metal. Trans.*, **24B** (1993), 481.
- (12) S. V. Semenovskaya: *Physica status solidi b*, **64** (1974), 291; S. V. Semenovskaya and D. M. Umidov: *Physica status solidi b*, **64** (1974), 627.
- (13) A. G. Khachaturyan: *Theory of Structural Transformations in Solids*, John Wiley, New York, (1983), 574.
- (14) W. L. Bragg and E. J. Williams: *Proc. Roy. Soc.*, **A145** (1934), 699; **A152** (1935), 231; J. G. Kirkwood: *J. Chem. Phys.*, **6** (1938), 70.
- (15) R. Kikuchi: *Phys. Rev.*, **81** (1951), 988; *J. Chem. Phys.*, **60** (1974), 1071.
- (16) E. M. Lifshitz: *Fiz. Zh.*, **7** (1942), 61, 251.
- (17) Y. A. Chang and J. P. Neumann: *Prog. Solid Stat. Chem.*, **14** (1982), 221.
- (18) S. V. Radcliffe, B. L. Averbach and M. Cohen: *Acta Met.*, **9** (1961), 169.
- (19) M. Weinlagen, B. Köhler, J. Wolff and Th. Hehenkamp: *Defect and Diffusion Forum*, **143–147** (1997), 449.