Revisiting the phenomenological model for effect of chemical ordering on diffusion

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ABSTRACT

The recently developed phenomenological model (Helander T, Ågren J. 1999.) in two-sublattice (2SL) formalism for describing the effect of chemical ordering on diffusion in bcc-B2 ordered alloys was carefully re-analyzed and validated to be applicable in ordered bcc-B2, fcc-L1$_0$ and fcc-L1$_2$ phases. The model was then extended into one in four-sublattice (4SL) formalism in a thermodynamically consistent way. With the more physically based 4SL model, different ordered structures (e.g., fcc-L1$_0$ and fcc-L1$_2$) with respect to the same disordered phase (e.g., fcc-A1) can be simultaneously described. In order to evaluate the reasonable "endmembers" in 4SL model when the first-principles calculations and/or sufficient experimental diffusivities are not available, the "pair activation energy" was proposed in the present work to a first approximation. The suggested phenomenological model in 4SL formalism together with the concept of "pair activation energy" was finally applied to describe diffusion in the ordered fcc-L1$_2$ phase of the binary Ni–Al system. Several advantages of using the 4SL model over the 2SL model were also demonstrated.

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1. Introduction

Materials with ordered intermetallics usually possess excellent thermal and mechanical properties, and are thus widely applied in industry as high-temperature structure materials, coatings, diffusion barriers, etc. One important type of such materials is bond-coat alloys for thermal barrier coatings (TBCs) in turbine blades, of which the microstructure usually contains ordered intermetallics [1], e.g., bcc ordered B2 (bcc-B2) and fcc ordered L1$_2$ (fcc-L1$_2$) phases. One key factor limiting the lifetime of TBCs is the inter-diffusion between the bond-coat and the Ni-based superalloy substrate. In order to assist the engineering-oriented lifetime assessment and even design new TBCs, reliable diffusivity data for ordered intermetallics is the prerequisite. However, such data cannot be estimated by simple extrapolation or interpolation of the sparse experimental data available in the literature, especially for the multicomponent materials in practice. Therefore, a general and efficient approach is needed to model and predict diffusivities in multicomponent ordered intermetallic phases.

Such an approach has recently been proposed by Helander and Ågren [2] and implemented in a software called DICTRA (DIffusion-Controlled TRAnsformation) [3]. The concept of "atomic mobility" was introduced in DICTRA software, and atomic mobilities for each phase are stored in databases instead of the sophisticated diffusivity matrix [4]. The atomic mobilities are represented by various physical/mathematic models, and the model parameters can be assessed on the basis of the limited experimental diffusivity data in the framework of the so-called CALPHAD (CALculation of PHAse Diagram) technique [5]. From the established atomic mobility database together with the thermodynamic database, one can calculate a variety of concentration-/temperature-dependent diffusivities and also perform quantitative one-dimension (1-D) simulation of diffusion-controlled phase transformations based on the local equilibrium hypothesis by means of DICTRA. What is more, the successful coupling of the phase-field method with the CALPHAD thermodynamic and atomic mobility databases in recent years definitely broadens the application of this method [6–10]. Up to now, several atomic mobility databases for disordered alloys and alloys with magnetic ordering have been developed for different multicomponent alloys, e.g. Fe-, Ni- and Al-based alloys [11,12].

However, there seems much remaining to be done for alloys with chemical ordering because of its complex nature.

Since the first experimental measurement of diffusivity in β brass by Kuper et al. [13], it has long been believed that a strong deviation from the usual linear behavior exists when plotting the temperature-dependent diffusivity in an Arrhenius diagram for alloys with a chemical order-disorder transition. This interesting phenomenon has attracted numerous experimental and theoretical investigations. One of the early work is from Girifalco in 1964 [14], who applied the Bragg-Williams theory and derived the conclusion that the activation energy for diffusion in AB-type bcc-B2 ordered alloys depends on the square of the long-range order parameter. Later, Tokei et al. [15] confirmed that Girifalco's derivation is also valid for AB3-type bcc-B2 ordered alloys. Based on the work from Girifalco [14] and Tokei et al. [15], Helander and Ågren [2] introduced an equivalent phenomenological model in the two-sublattice (2SL) formalism to describe the atomic mobilities in binary bcc-B2 phases, and later generalized into multicomponent systems [16]. In addition, Helander and Ågren [2,16] have also applied this phenomenological model to successfully establish the atomic mobility databases in bcc-B2 alloys of the Fe—Al, Ni—Al and Fe—Al—Ni systems, from which various diffusion properties were also simulated. Very recently, Campbell [17] initiated the use of this phenomenological model to study also diffusion in the ordered fcc-L1$_2$ phase in Ni—Al and Ni—Al—Cr alloys, and the corresponding atomic mobility databases were successfully developed. Soon after that, the present authors [18] tried the same phenomenological model from Helander and Ågren [2] to describe diffusion in the ordered fcc-L1$_2$ phase of the Ni—Al system by taking the homogeneity range and defect concentration into account and as a result were able to use less parameters. Though both sets of the resulted atomic mobility databases for the fcc-L1$_2$ phase in the Ni—Al system from Campbell [17] and Zhang et al. [18] can describe the experimental diffusion properties reasonably well, very different model parameters were employed. The seemingly arbitrary selection of model parameters has since posed a question for us: Is the phenomenological model developed for the ordered bcc-B2 phase by Helander and Ågren [2] also applicable for other ordered phases, e.g. fcc-L1$_2$ and fcc-L1$_0$?

Moreover, a detail literature survey suggests that three more papers have been published by Girifalco and his colleague in 1968 [19—21] after his paper in 1964 [14]. In the first one of the three later papers, Schoijet and Girifalco [19] pointed out the shortcomings and errors made in the paper by Girifalco in 1964 [14], and applied more elaborate theories to obtain the activation energy for diffusion in bcc-B2 ordered alloys, though its formula is similar to that one derived by Girifalco in 1964 [14] if neglecting the effect of short-range ordering. While in the other two papers, Schoijet and Girifalco [20,21] presented the activation energy for diffusion in both fcc-L1$_0$ and fcc-L1$_2$ ordered phases. These information are extremely important for validating the reliability of the phenomenological model developed by Helander and Ågren [2] in different ordered phases.

In addition, as is well known, the four-sublattice (4SL) model is more physically based for describing the bcc or fcc-based order-disorder transitions than the 2SL model because the 4SL model reflects exactly the crystal structures, and can simultaneously represent different ordered structures (e.g., fcc-L1$_0$ and fcc-L1$_2$) with respect to the same disordered phase (e.g., fcc-A1). With the ever increasing computing power of modern computers, more and more order-disorder thermodynamic descriptions are in 4SL formalism today [22,23]. However, there is still no any phenomenological model in 4SL formalism for describing the effect of chemical ordering on diffusion. Thus, there is an urgent need to extend the phenomenological model in 2SL formalism into one in 4SL formalism.

In the following section, we will first present two definitions of the long-range order parameter, which describes the degree of the chemical ordering. In Section 3, the original models for the activation energy in bcc-B2, fcc-L1$_0$, and fcc-L1$_2$ ordered phases reported by Schoijet and Girifalco [19—21] are briefly introduced. After that, we will present the phenomenological model from Helander and Ågren [2] in 2SL formalism, and validate its consistency with the original models by Schoijet and Girifalco [19—21] in different ordered phases in Section 4. Furthermore, a phenomenological model in 4SL formalism will be proposed, and the equivalence between the model parameters in 4SL and 2SL formalisms will also be derived. In Section 5, the proposed phenomenological model in 4SL formalism will be applied to reassess the atomic mobility parameters in fcc-L1$_2$ phase of the Ni—Al system. The calculated diffusion properties based on the mobilities in 4SL formalism will be compared with the previous ones based on the mobilities in 2SL formalism [18]. Finally, the conclusions will be drawn in Section 6.

2. Definitions of long-range order parameter

The long-range order parameter S is a logical measure of the degree of chemical ordering. Several definitions of S are available in the literature. Assuming an ordered phase described by a 2SL model $(\mathbf{A}, B)^{\alpha}(A, \mathbf{B})^{\beta}$ (here, the major constituent on each sublattice is highlighted in bold case), the definition of S accepted by Helander and Ågren [2] is

$$S = P_A^{\alpha} - P_A^{\beta} = P_B^{\beta} - P_B^{\alpha}, \tag{1}$$

where P_i^{α} and P_i^{β} are the probabilities of finding an i (i.e., A or B) atom on an α and β site, respectively. While the one utilized by Girifalco and his colleague [14,19—21] gives

$$S = \frac{(N_{A\alpha}/N_{\alpha}) - (N_{\alpha}/N)}{1 - (N_{\alpha}/N)} = \frac{(N_{B\beta}/N_{\beta}) - (N_{\beta}/N)}{1 - (N_{\beta}/N)}, \tag{2}$$

where $N_{A\alpha}$, $N_{B\beta}$, N_{α}, N_{β} and N are numbers of A atom on α site, B atom on β site, α, β, and all sites, respectively. Actually, $(N_{A\alpha}/N_{\alpha})$ in Eq. (2) equals to P_A^{α} in Eq. (1), while $(N_{B\beta}/N_{\beta})$ equals to P_B^{β}. Based on the definition (2), Schoijet and Girifalco [19—21] gave the following relations: $P_A^{\alpha} = P_B^{\beta} = (1 + S)/2$ and $P_B^{\alpha} = P_A^{\beta} = (1 - S)/2$ for both bcc-B2 and fcc-L1$_0$ phases, while $P_A^{\alpha} = (3 + S)/4$, $P_B^{\alpha} = (1 - S)/4$, $P_A^{\beta} = 3(1 - S)/4$, and $P_B^{\beta} = (1 + 3S)/4$ for fcc-L1$_2$ phase. It should be pointed out that the definition (2) used by Schoijet and Girifalco [14,19—21] is only applicable for perfect crystals, i.e., at the exact stoichiometric composition.

3. Original models

Based on the observation of shortcomings and errors in the paper published by Girifalco in 1964 [14], Shoijet and Girifalco [19—21] employed Kirkwood's theory and quasi-chemical theory and derived a new expression for the activation energy of diffusion in ordered bcc-B2, fcc-L1$_0$ and fcc-L1$_2$ phases by including also the short-range ordering effect. Their derived general activation energy for species k in ordered bcc-B2 or fcc-L1$_0$ phase is given as [19,20]

$$Q_k = Q_k^0 + A_1^k S^2 + \frac{A_2^k (1 - S^2)^2}{RT}, \tag{3}$$

where Q_k^0 is the activation energy for k in completely disordered state. Both A_1^k and A_2^k are constants. S is the long-range order parameter. R is gas constant and T absolute temperature in Kelvin.