Intermetallics 44 (2014) 60–63

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Cluster expansion approach for modeling strain effects on alloy phase stability

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ARTICLE INFO

Article history:
Received 13 May 2013
Received in revised form
24 July 2013
Accepted 19 August 2013
Available online 19 September 2013

Keywords:
A. Intermetallics, miscellaneous
B. Phase diagrams
E. Ab-initio calculations

ABSTRACT

We demonstrate applicability of the proposed extended cluster expansion (CE) technique, enabling complete representation of strain effects on alloy configurational energy on single and multiple lattices. Complete and orthonormal basis function to describe configurational energy is constructed in terms of spin variable ω on virtual lattice and σ on base lattice, where the former specifies the strain of a given cell from the base cell. We estimate formation energy of superlattice composed of alternate stacking of ordered structures for Cu–Au binary alloys where the strain effects should play significant role. The proposed CE is shown to precisely estimate the strain effects on total energy for alloys, which cannot be essentially handled by the current CE.

1. Introduction

In order to effectively design suitable alloy materials in terms of narrowing down the controlling parameters, knowing the alloy configurational thermodynamics and the relationship between the property and structure is a fundamental prerequisite since structures of alloys, including atomic arrangements and compositions, should significantly affect their physical properties. However, consideration of a tremendous number of atomic arrangements should be required to quantitatively predict alloy thermodynamics or to capture characteristic properties in configuration space, which is typically far beyond the practical limitation of density functional theory (DFT) calculations. Therefore, in order to reduce the computational cost of DFT, alternative approaches have been proposed, which can be combined with DFT calculation. One of the most promising and well-established approaches is the cluster expansion (CE) technique [1], which provides an accurate prediction of configuration-dependent scalar properties including internal energy and elastic constants. There has been wide applications for CE combined with DFT to variety of systems: Construction of phase diagrams for binary and multicomponent alloys, surface ordering and segregation with existence of molecular adsorption, ground-state atomic configuration for alloy nanoparticles, effects of lattice vibration and of pressure on phase stability, and the comprehensive search for superhard materials [2–7]. The CE has been modified in various manners for systems requiring specific treatments in terms of configuration spaces: formation energy for long-period superlattices is effectively handled by mixed-space CE [8], and tensor-valued properties, such as elasticity and dielectric constants, can be handled by tensorial CE [9]. Thus, CE has become a powerful tool to theoretically optimize alloy materials in terms of atomic arrangements [10].

However, in order to model more general configurational energetics, the current CE still has essential problem: strain effects on total energy, ΔE_S, cannot be handled by the CE. Laks et al. first pointed out this problem [8], and they propose mixed-space CE where ΔE_S is treated as a correction term of CE in terms of composition. Their proposed approach of ΔE_S is however confined to a given single lattice where a CE Hamiltonian is constructed, since CE Hamiltonian itself depends on a single given lattice. Recently, the author developed an extended CE, variable-lattice CE (VLCE) [11–13] that can handle multiple lattices in a single Hamiltonian and then we extended VLCE, continuous-spin basis VLCE (CS-VLCE) [14] which can handle ΔE_S not as correction term: ΔE_S can be completely described in terms of complete basis functions. CS-VLCE can also treat ΔE_S on single as well as multiple lattices, which cannot be essentially achieved by the current CE. In the present study, we demonstrate an applicability of CS-VLCE to prediction of superlattice formation energies consisting of ordered structures, where ΔE_S should play significant role. In the following sections, we first briefly describe construction of CE, VLCE and CE-VLCE Hamiltonian for single and multiple lattices, and then, we show the application of CS-VLCE to Cu–Au binary alloys.

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http://dx.doi.org/10.1016/j.intermet.2013.08.010

2. Methodology

We first briefly introduce construction of CE Hamiltonian. Let us consider the system where occupation of lattice point i in a given lattice having N lattice points is described by Ising-like pseudospin variable, σ_i. Then an N-dimensional vector $\vec{\sigma} = \{\sigma_1, \sigma_2, \cdots, \sigma_N\}$ can uniquely specify any atomic arrangement on the lattice points. Under this definition, any configuration property f (e.g., internal energy) depending on the atomic arrangement can be expressed by the complete orthonormal basis functions of the atomic arrangement $\vec{\sigma}$, which are called cluster functions Ψ:

$$f(\vec{\sigma}) = \sum_{\alpha,(M)} \left\langle f(\vec{\sigma}) \middle| \Psi_\alpha^{(M)}(\vec{\sigma}) \right\rangle \Psi_\alpha^{(M)}(\vec{\sigma}), \tag{1}$$

where $\langle | \rangle$ represents the inner product in σ space and called the effective cluster interaction (ECI) on cluster α composed of the lattice points and (M) denotes basis functions. Complete and orthonormal basis at each lattice point, ρ, can form the basis function Ψ by applying the following Gram-Schmidt technique to linearly independent polynomial set $\{1,\sigma,\sigma^2,\ldots,\sigma^{R-1}\}$ for an R-component system:

$$\begin{aligned}
\rho_m(\sigma_i) &= \frac{b_m(\sigma_i)}{\langle b_m(\sigma_i) | b_m(\sigma_i)\rangle^{1/2}} \\
b_m(\sigma_i) &= \sigma_i^m - \sum_{j=0}^{m-1} \left\langle \rho_j(\sigma_i) \middle| \sigma_i^m \right\rangle \rho_j(\sigma_i) \quad (m \neq 0) \\
b_m(\sigma_i) &= 1 \quad (m = 0),
\end{aligned} \tag{2}$$

where m takes integer values from 0 to $R-1$. Complete and orthonormal basis functions for whole lattice points, Ψ, can therefore be obtained by taking tensor product of vector space for each lattice points. It is now clear that the f on different lattices cannot be handled by conventional CE with a single formalism, since spin variable σ_i itself does not contain any information about the position of lattice point i.

In VLCE, multiple lattices are linked via a combination of two lattices of "base" and "virtual" lattices in order to simultaneously treat atomic arrangements on multiple lattices. The occupation of elements on a certain given lattice is specified by the base lattice, which is similar to conventional CE. The position of individual lattice points or a set of lattice points measured from the base lattice is specified by the virtual lattice. Therefore, the base lattice is a real lattice, while the virtual lattice is merely an abstract lattice which does not include a concrete concept of symmetry. A standard orthonormalization technique used in CE described in Eq. (2) can form the basis function for base and virtual lattices, and taking the tensor product of vector space for base and virtual lattices leads to a general VLCE expression for property f: [11]

$$\begin{aligned}
f(\vec{\sigma}, \vec{\tau}) &= \sum_{\alpha,\beta} \sum_{(M,L)} \Phi_{\alpha;\beta}^{(M,L)}(\vec{\sigma}, \vec{\tau}) V_{\alpha;\beta}^{(M,L)} \\
\Phi_{\alpha;\beta}^{(M,L)}(\vec{\sigma}, \vec{\tau}) &= \prod_{\substack{i \in \alpha \\ d \in (M)}} \phi_d(\sigma_i) \prod_{\substack{p \in \beta \\ d' \in (L)}} \phi_{d'}(\tau_p),
\end{aligned} \tag{3}$$

where Φ is an expansion function, and is called a cluster function. α and β represent clusters consisting of lattice points i and p on base and virtual lattices, and (M) and (L) specify the combination of basis function index d and d' on base and virtual lattices, respectively. σ and τ are spin variables on base and virtual lattices, and individually have values to specify the occupation of elements or the position of lattice points, which are similar to spin variables in the Ising model.

Next, we see the essential problem of CE for treating strain effects on total energy shown by Laks et al. [8] We take an example of one-dimensional long-period superlattice along a certain direction, which is composed of alternating elements A and B with repeat period p. Under the condition of different lattice parameters of A and B, the formation energy of the superlattices in terms of pure A and B should have finite and positive value when p goes to infinity due to the strain energy coming from lattice size mismatch. However, at $p \to \infty$, they show that the CE formation energy with finite number of basis function should always be zero. The reason is: CE interprets a certain A atom far from the interface between A and B as A atom in bulk A with lattice parameter same as pure A, since finite number of CE basis connects the A atom with other A atoms. The similar interpretation holds for B atoms. The superlattice at $p \to \infty$ is therefore interpreted as a sum of non-interacting bulk A and bulk B, which leads to zero formation energy. This problem not only occurs for superlattice consisting of pure A and B, but also for that of ordered structures with different lattice parameters. Thus, the CE completely misses the strain effects for a long-period superlattice. The same problem also occurs in VLCE, since VLCE basis functions defined on a single lattice have essentially contain the same amount of information about structure as those in CE for the same single lattice [11]. In order to avoid this problem, the strain effect on total energy, ΔE_S, is treated as correction term in the mixed-space CE (MSCE): [8]

$$E(\vec{\sigma}) = \sum_{\alpha,(M)} V_\alpha^{(M)} \Psi_\alpha^{(M)}(\vec{\sigma}) + \sum_{\mathbf{k}} \frac{\Delta E_\mathrm{CS}}{4x(1-x)} |S(\mathbf{k}, \vec{\sigma})|^2, \tag{4}$$

where the first term on the right-hand side corresponds to the current CE expression, and the second is the correction term for the strain effect, ΔE_S. ΔE_CS is called the constituent strain energy obtained by taking the composition average of strain energy required to deform bulk A and B biaxially to the plane parallel to the interface, x is the composition of the system. S is defined as

$$s_j(\vec{\sigma}) = \sum_{\mathbf{k}} S(\mathbf{k}, \vec{\sigma}) \exp(-i\mathbf{k} \cdot \mathbf{R}_j), \tag{5}$$

where $s_j(\vec{\sigma})$ denotes spin variable on lattice point j in configuration $\vec{\sigma}$, $\mathbf{R}_j$ denote position of lattice point j, and summation over $\mathbf{k}$ runs over the first Brillouin zone. The second term is derived by performing a reciprocal space cluster expansion to obtain constituent strain energy in powers of x at the first order. The important points are (i) expression of energy, $E(\vec{\sigma})$, should not be complete in configuration space since the second term in right-hand side of Eq. (4) is an approximation in terms of x, and (ii) application of the correction term for strain effects is confined to a single given lattice where the CE Hamiltonian is constructed, since the second term is derived from conventional CE. In order to overcome the problems of (i) and (ii), further modification should therefore be required so that the strain effect can be included in a complete basis functions on multiple lattices, which will be achieved by the CS-VLCE in the followings.

Since the spin variables of CE or VLCE merely have information about atomic arrangements or displacements from the base lattice in terms of internal position of the defined cell, they cannot essentially handle ΔE_S. Therefore, our strategy to include ΔE_S is the use of virtual lattice which describes deformation of cell from an certain defined cell (hereafter referred to as the base cell). The concept of the base cell and corresponding definition of the virtual lattice is schematically illustrated for a 2-dimensional lattice in Fig. 1. In Fig. 1, introduced spin variable ω on corresponding virtual lattice points of i and j, can completely describe any deformation of the cell from the base cell, which is a similar definition of spin