FIRST-PRINCIPLES CALCULATIONS RESULTS IN PHASE DIAGRAM CONSTRUCTION

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Abstract

Evaluation of lattice stabilities of metastable phases is for a long time the frequently addressed problem in thermodynamics for phase diagram calculations. Recent development of ab initio calculations makes it possible to use the total energy difference between pure element metastable structure and standard element structure for phase diagram construction also for complex intermetallic phases.

The physical model of sigma-phase is proposed and tested on the Fe-Cr system, using data from literature for remaining phases. The model is based on the two sublattice model as for solid solution phase, but the structure energy difference for pure components ($\Delta E_{\text{tot},\sigma}^{\text{SER}}$) is based on the results of calculations of electronic structure from the first principles (Full Potential Linear Augmented Plane Wave – FLAPW - method). Entropy part of Gibbs energy of elements in sigma-phase structure and of excess Gibbs energy of mixing of sigma-phase have to be still adjusted to phase equilibrium data. Extension of the model to other complex intermetallic phases is proposed.

Keywords: first-principles, thermodynamics, intermetallics, phase diagrams

1. Introduction

The increasing use of thermodynamic phase diagram calculations and the establishment of thermodynamic databases needs the reliable data
for lattice stability of metastable phases of elements because phase equilibria calculations performed by CALPHAD method (CALculation of PHAse Diagrams) are based on a description of Gibbs energy of phases by means of mathematical expressions (models) containing lattice stabilities of all components in studied phases[1,2]. These values can be based on various sources: for stable phases the data can be measured and assessed, taking into account the phase equilibrium data. For metastable phases, the assessment can be based on the relationship between entropy of fusion, melting point and crystal structure, periodic group trends and stacking fault energies can be taken into account [3]. Recently, the first-principles electronic structure calculations results exhibit increasingly successful predictive capability and they are to be given more attention [4,5].

Lattice stabilities for many elements in simple structures (FCC, BCC, HCP) were assessed successfully by the concentrated effort of Scientific Group of Thermodata Europe (SGTE) and can be found in [6]. The ab initio calculations results for metastable structure cannot give full agreement with assessed values of Gibbs energies, because former are related to $T=0 \text{ K}$ and extrapolation of later to $T=0 \text{ K}$ is not reliable, because many metastable structures are unstable in fact, so the entropy value cannot be defined exactly [7].

Data for lattice stabilities of complex structures are lacking at all. We have chosen the sigma-phase as an example of complex structure, to demonstrate the problems to be solved. Sigma-phase (5 inequivalent lattice sites, 30 atoms per repeat cell) is one of such complex structures. It is a special kind of intermetallic phase, which exists in transition metal systems in a restricted concentration region, similarly as chemical compounds, and which has a large concentration range of stability, similarly as solutions. In the Fe-Cr system sigma-phase was first described by Bain [8] and the phase equilibria with bcc-phase were determined by Cook and Jones [9]. Recently, Villars et.al [10] has reported 110 intermetallic phases with sigma-phase structure.

For its modelling in the framework of CALPHAD method, it is necessary to know the structure energy difference between standard Gibbs energy of that phase (which is for any pure component hypothetical) and of Gibbs energy of its stable element reference state (SER) for every
element concerned. The aim of this paper is to show how the ab initio electronic structure calculations can contribute to solution of this task.

2. Standard Gibbs energy determination of sigma-phase for CALPHAD method Sigma-phase as bcc-based structure

First attempt to calculate the phase diagram with sigma-phase in Fe-Cr system by Kaufman and Nesor [11] considers the sigma-phase as a bcc base stoichiometric compound with $\Delta H^E = 4867 \text{ J mol}^{-1}$ and $\Delta S^E = 7.097 \text{ J mol}^{-1} \text{ K}^{-1}$ for $x_{Fe} = 0.53$. Later, Müller and Kubaschewski [12] calculated the phase diagram of Fe-Cr on the basis of critically evaluated thermodynamic properties of phases with $\Delta G^E$ expressed using experimentally determined $\Delta H^E (4749 - 5104 \text{ J mol}^{-1})$ and $\Delta S^E (1.4815 - 1.7745 \text{ J mol}^{-1} \text{ K}^{-1})$ for $x_{Fe} [0.49-0.57]$. The bcc structure was taken as a standard state for sigma-phase in both cases and, therefore, the experimental values of $\Delta H^E$ and $\Delta S^E$ were taken. This approach ignored the real structure of sigma-phase. Therefore, the attempts to determine the structure energy difference between Gibbs energy of sigma-phase and that of SER-phase were started.

3. Lattice stability of sigma-phase

First attempt to guess the lattice stability of sigma-phase was performed by Allibert et.al. [13], by extrapolating the experimental values of thermodynamic properties from relative narrow solution region to the pure components (end-members) in order to give a reasonable structure energy difference value.

The structure energy difference listed in their paper was:

Fe: $^o G^\text{sigma} - ^o G^\text{bcc} = 4603.28 + 0.22259^o T$

Cr: $^o G^\text{sigma} - ^o G^\text{bcc} = 2509.77 + 3.23^o T$

The extrapolations differed one from another, when various systems containing the chosen pure component were taken in consideration. The results for various binary systems had to be averaged and such extrapolation over a great deal of phase diagrams is again questionable.
4. Sublattice model of sigma-phase

To overcome this difficulty, the sublattice model for sigma-phase was proposed by Anderson and Sundman [14], which creates the expression for standard Gibbs energy of sigma-phase, starting from the detected structure of sigma-phase (5 inequivalent lattice sites), comparing it with the standard Gibbs energy of real structures of pure metals in question. This model of standard Gibbs energy of sigma-phase is empirical containing adjustable parameters, which are determined by fit to all available experimental data. This procedure was summarised in Ringberg workshop 1996 [9]. As an example, the formula for sigma-phase was obtained as $B_8(A,B)_{18}A_4$ [14] or later $(A,B)_{10}(A,B)_{16}A_4$ [15].

The values of Gibbs energy parameters for 8:18:4 model sigma-phase in Fe-Cr system result from adjustment to phase equilibrium data as follows:

$$\begin{align*}
\Delta G^{\text{FeCrCr}}_{\text{sigma}} &= 8 \Delta G^{\text{FCC}}_{\text{Fe}} + 22 \Delta G^{\text{BCC}}_{\text{Cr}} + 49000 - 31.0^\circ \text{T}; \\
\Delta G^{\text{FeCrFe}}_{\text{sigma}} &= 8 \Delta G^{\text{FCC}}_{\text{Fe}} + 4 \Delta G^{\text{BCC}}_{\text{Cr}} + 18 \Delta G^{\text{BCC}}_{\text{Fe}} + 72000 - 31.0^\circ \text{T}.
\end{align*}$$

Other thermodynamic data were taken from Anderson and Sundman's paper [14], with improved liquid phase description by Lee [16]. Fig. 1 shows the agreement of calculated phase equilibrium data with experimental ones achieved for Fe-Cr system, as an example. The corresponding values of Gibbs energies of phases at 1000 K are shown in Fig 2.

![Fig. 1 Calculated phase diagram of Fe-Cr system according to the sublattice model of sigma-phase, compared with experimental values of various authors: (*) Cook and Jones [9], (Δ) Adcock [21], (◊) Hellawell and Hume-Rothery [22], (▾) Bungardt et al. [23], (◇) Baerleken et al. [24], (+) Nishizawa [25]. Thermodynamic data for fcc and bcc phases were taken from [14], data for liquid from [16].]
It needs to be mentioned that physical background of the proposed procedure of modelling is not fully exact, "it has been defined by convenience"[14]. It only enables us to approximate the lattice stability of metastable phase of pure component by means of linear combination of the known Gibbs energy of stable phases of pure components (elements) with the same coordination numbers. This makes it possible to express Gibbs energy of standard state of sigma phase, but the Gibbs energy has to be adjusted to phase equilibrium data for a compositions far away from the pure end-members and therefore its physical reliability is again questionable. Both, the energy and the entropy, has to be adjusted in unknown ratio in this procedure. It is also no longer possible, within this model, to find the value of the Gibbs energy for a composition corresponding to either pure A or pure B. Further, it is known from X-ray studies [10], that the mixing of components takes place to some extent in all sublattices. Proposed model does not respect this fact [15].

One of the most significant shortcomings of the described method of Compound Energy Formalism (CEF) is the restriction of the entropy of mixing to that of an ideally random mixture. This assumption is contained also in the paper of Pratt and Jones [17], who used pair-wise interaction model for the description of the sigma-phase. By the restriction to randomness, the short range order (SRO) is ignored and a part of the contribution of SRO to Gibbs energy is hidden in the “excess term” after the adjustment of parameters to experimental data. Better description of
SRO can be achieved by Cluster Variation Method (CVM) of configurational entropy and by Cluster Expansion Method (CEM) of the mixing energy. The application of mentioned methods in CALPHAD treatment is promising, but not yet commonly used.

Furthermore, it is necessary, as was mentioned above, to take into account, that the metastable structures can be completely unstable. This is the case e.g. for fcc Cr, fcc Fe and bcc Co which follows from the calculation of total energy from the first-principles along trigonal or tetragonal deformation path [18]. In the case of unstable structures the instability with respect to some vibrational mode has the consequence, that the entropy and therefore also Gibbs energy is not exactly defined. To the best of our knowledge, it is not known for sigma-phase structure whether it is metastable or unstable, so the entropy value should be preliminary regarded as “effective”.

5. Results and Discussion

5.1. Physical model of sigma-phase

The ab initio computations of the total energies of complex phases had been addressed recently. The structure energy difference, calculated by FLAPW (Full potential augmented plane wave) method enable us to use full physical information about sigma-phase (based on X-ray results) and to re-use the old model [13] for its thermodynamic description. Knowledge of the correct value of total energy difference between sigma phase and SER state phase of end-members from first-principles calculations makes it possible to build the Gibbs energy difference of pure components (lattice stability) on physically correct energetic base. The entropic term should be adjusted to phase equilibrium data only.

The Gibbs energy values for real sigma-phase alloy could be calculated for continuously varying composition of sigma phase by interpolation of the results of total energy calculations performed for discrete compositions. But the interaction parameters L, necessary for \( G^{E,\text{sigma}} \) description, are to be adjusted to phase equilibrium data.

Finally, the proposed model is based again on the two sublattice model, similarly as for solid solution phase, but as mentioned above the
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Structure energy difference for end-members \( (\Delta E_{\text{tot},i}^{\text{sigma-SER}}) \) is based on the results of calculations of electronic structure from the first-principles mentioned above. The Gibbs energy of the sigma-phase may be then expressed by means of the known relation:

\[
G_m^{\text{sigma}} = \sum_i x_i \sigma G_i^{\text{sigma}} - T S_m^{\text{ideal}} + G^E, \tag{1}
\]

where

\[
\sigma G_i^{\text{sigma}} = \sigma G_i^{\text{SER}} + \Delta E_{\text{tot},i}^{\text{sigma-SER}} - T S_i^{\text{vib},\text{sigma}} \tag{2}
\]

\[
S_m^{\text{ideal}} = -R \sum_i (x_i \ln x_i) \tag{3}
\]

\[
G^E = x_i x_j (\sigma L_{i,j}^{\text{sigma}} + \sigma L_{i,j}^{\text{sigma}} (x_i - x_j)) \tag{4}
\]

This procedure gives a physical meaning to parameters of the mathematical expression for Gibbs energy difference between the energy of a hypothetical sigma-phase structure of end-members and of the Gibbs energy of its standard element reference state. So, the knowledge of the total energy difference between pure elements in the sigma phase structure and in other relevant structures gained by ab initio calculations could substantially simplify the physical modeling of the thermodynamic properties of the sigma phase (and other relevant intermetallic phases) in the CALPHAD method (two sublattice only could be used) giving to that thermodynamic properties correct physical background. Preliminary results of total energy calculation (based on the calculations at experimental volume – calculations at equilibrium volume are in progress) lead to the evaluation of the total energy difference between sigma-phase and SER-phase at 0 K [19]:

\[
\Delta E_{\text{tot,Fe}}^{\text{sigma-SER}} = 40300 \text{ J.mol}^{-1}
\]

\[
\Delta E_{\text{tot,Cr}}^{\text{sigma-SER}} = 20300 \text{ J.mol}^{-1}
\]

The value of \( S_i^{\text{vib}} \) should be adjusted to phase equilibrium data only, supposing a metastable sigma-phase structure. In the case of an unstable structure the value of \( S_i^{\text{vib}} \) adjusted to experimental phase data could be
regarded as “effective” value. The best way we propose for the unification of $S_{\text{Vib, \sigma}}$ gained by optimisation of various systems is to start with the prototype sigma-FeCr, and further optimise stepwise entropy term by means of $\Delta E_{\text{tot,i, \sigma}} - \text{SER}$ for other elements i (optimise entropy term for only one element i in every new binary system).

The value of $G^E$ could than be expressed by a polynomial (e.g. Redlich-Kister – eq.(4)), taking into account SRO. First-principle calculations at 0 K yield the concentration dependence of $E_{\text{tot}}$ for sigma-phase in various systems. Such results could be found e.g. in [19] and [20] – made within a simpler Linear Muffin-Tin Orbital Method in Atomic Sphere Approximation (LMTO-ASA) - and could be used as a starting guess for the adjustment to phase equilibrium data. It needs to be mentioned that the $G^E$ in eq.(1) consists of $E_{\text{tot}}(x)$ and of the expression $T.S$, where $S$ contains both entropy of configuration and of vibration of the sigma-phase alloy. To test the preliminary total energy calculations results by phase diagram calculation the values of thermodynamic functions were taken again from Anderson and Sundman’s paper [14], with improved liquid phase description by Lee[16], for Fe-Cr system. Actual values of Gibbs energy differences for sigma-phase structure of elements and values of excess Gibbs energy parameters (see eq.(4)) are given below.

\[
\begin{align*}
\text{Fe: } \quad ^oG^{\sigma} - ^oG^{\text{bcc}} &= +40300; \\
\text{Cr: } \quad ^oG^{\sigma} - ^oG^{\text{bcc}} &= +20300; \\
^oL^{\sigma}_{\text{Cr,Fe}} &= -111400. \\
^1L^{\sigma}_{\text{Cr,Fe}} &= +46000.; \\
^2L^{\sigma}_{\text{Cr,Fe}} &= -92000.;
\end{align*}
\]

Phase diagram calculations using the sigma-phase description in terms of the proposed model and ab initio results yield equally good agreement with experimental data as the sublattice model. It is shown for Fe-Cr system in Fig.3, for example. Thermodynamic Gibbs energy functions describing Fe-Cr system in proposed model are shown in Fig.4. Extension to the ternary system was tested succesfully.
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Fig. 3 Calculated phase diagram of Fe-Cr system according to the physical model of sigma-phase, compared with experimental values of various authors:
* - Cook and Jones [23],
Δ - Adcock [21],
- Hellawell and Hume-Rothery [22],
◊ - Bungard et al. [23],
▽ - Baerlecken et al. [24],
+ - Nishizawa [25].
Thermodynamic data for fcc and bcc phases were taken from [14], data for liquid from [16].

Fig. 4 Gibbs energy of phases in the Fe-Cr system at 1000 K according to the physical model of sigma-phase:
1 – liquid,
2 – bcc,
3 – fcc,
4 – sigma

6. Conclusion

Recent development of ab initio calculations enable us to calculate the total energy difference between pure element metastable structure and standard element structure for phase diagram construction also for complex intermetallic phases. This was used in proposal of the physical
model of sigma-phase which was tested on the Fe-Cr system, using data from literature for remaining phases. The proposed model is based on the two sublattice model as for solid solution phase. The structure energy difference for pure components ($\Delta E_{\text{tot},i}^{\text{sigma-SER}}$) is calculated from the first principles (Full Potential Linear Augmented Plane Wave – FLAPW method). Entropy part of Gibbs energy of elements in sigma-phase structure and of excess Gibbs energy of mixing of sigma-phase have to be still adjusted to phase equilibrium data.

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